

# Properties of Complex Inorganic Solids

Edited by

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## PREFACE

It is common practice today to use the term "alloy" in connection with specific classes of materials, with prominence given to metals and semiconductors. However, there is good justification for considering alloys in a unified manner based on properties rather than types of materials because, after all, to alloy means to mix. The scientific aspects of mixing together different materials has a very long history going back to early attempts to understand and control materials behavior for the service of mankind.

The case for using the scientific term "alloy" to mean any material consisting of more than one element can be based on the following two considerations. First, many alloys are mixtures of metallic, semiconducting, and/or insulating materials, and the properties of an alloy, i.e., metallic, semiconducting, or insulating, are often functions of composition and of external conditions, such as temperature and pressure. Second, and most importantly, in attempting to understand the various properties of materials, whether physical, chemical, or mechanical, one is apt to use the terminology and experimental, formal, and computational methods in their study that transcend the type of material being studied.

Specialization in science, of course, is necessary and unavoidable as the complexity of phenomena that come increasingly under study escalates, and as our abilities to study nature at deeper and deeper levels increase. The result may be viewed as a loss by some: the progressive loss of general perspective, and ultimately a loss of the underlying commonality of purpose and methodology that properly underlies scientific activity in general. This is evident in the different languages that have evolved over the years to describe essentially the same thing within different scientific specializations. A mineralogist's solid solution component is a physicist's dopant and a chemist's and materials scientist's impurity. The chemist, living in the world of finite molecules may have difficulty communicating with the physicist who insists on treating infinite systems. Both may find mineral names weird, wonderful, and funny. And yet the mineralogist's purpose is to arrive at a nomenclature as unambiguous as possible using the end-member name+solid solution and crystal structure topology.

In our view, there is much to be gained now by bringing these disparate factions back together. By sharing our experiences in our respective specializations, we gain fresh perspectives, and can develop new, integrated approaches to the study of natural phenomena. To be sure, the process of bridging the interdisciplinary gap is not easy, and will be greatly aided by tolerance and a sense of humor.

The basic purpose of the present conference and those to follow is to break down barriers to communication across disciplines and to foster, promote, and enhance a concerted and unified approach to the study of materials properties, cutting across types of materials and placing the emphasis where it belongs--on the properties themselves. A few examples may serve as illustration. The fundamental nature of electronic transport does not change qualitatively from Cu, to Si, to MgO, to Pyrochlore. To be sure, there are quantitative differences in the electrical conductivity among these substances and a conference on the electrical conductivity of metals is a more usual occurrence than one on wide gap insulators. But, as any mineralogist will tell you, conductivity measurements on minerals--which are mostly oxides and hence insulating--can reveal a great deal about

their internal properties and provide guidance in their utility. Other, specific properties commonly associated with metallic systems, such as superplasticity, also occur in ceramics and have important technical ramifications. The use of the Ising model to study the energetics and the stability of competing phases in multicomponent systems is by no means confined to metals or semiconductors but is also applied to minerals. As a further example, we may consider the formal methods developed for the study of alloy phase stability, primarily with respect to metallic and semiconducting systems. These methods conceivably can be expanded to apply to ceramics and minerals. In addition, traditional techniques applied by mineralogists to low symmetry and multicomponent crystalline systems are of increasing interest to ceramists and other materials scientists. Therefore, a derivative purpose of this conference is to help practitioners, both experimentalists and theorists, across the various scientific disciplines involved in the study of complex inorganic solids learn from one another, enhancing their own perspectives and horizons as well as those of their colleagues. It is this aspect of the conference which we hope to emphasize in subsequent meetings to a much greater extent than materialized in IAC-1.

It is our hope that promoting such an integrated approach to materials in the solid state can have serious and welcome consequences. We believe that this is a healthy response to the present and rapidly changing political and financial situation in the scientific enterprise which has seen funding for basic and often applied research dwindling down to insignificance. At the same time new and exciting areas of inquiry become more and more evident, such as environmental clean-up and restoration and preservation, and industry's--and the public's--need for miniaturization and friendly while powerful and accurate devices, to mention only a couple. It may open the possibility to apply methods and techniques established in one field to a different field, thus opening the door to innovative proposals for funding. The materials scientist, the metallurgist, the solid state physicist, the mineralogist, and the chemist of yesterday have a great deal to offer to these new fields of endeavor. It seems that a biennial *International Alloy Conference* (IAC), based on properties rather than classes of materials, can serve a vital purpose in the scientific community.

The following pages include the proceedings of the First International Alloy Conference, IAC-1, held in Athens, Greece, June 16-21, 1996. We have divided the material in the proceedings according to the four distinct sections used in the actual presentations, namely: characterization and phase stability, electronic structure and transport, mechanical properties, and multiple scattering theory and applications. Each of these is further divided in parts, where appropriate, containing materials closely related in content. At this point it is important to emphasize that IAC-1, and hence the proceedings, would not have materialized without the efforts of a number of colleagues, such as the members of the scientific and executive committees, who embraced the project and made invaluable suggestions regarding speakers and content. A great deal of gratitude is owed to Ms. M. Besheri and her team for the administrative and secretarial assistance her office provided, including hotel bookings and other arrangements. We also thank Ms. P. Vann and her staff at Plenum for their patience and their help in the publication of this volume.

A. Gonis  
A. Meike  
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## **CHARACTERIZATION AND PHASE STABILITY**

## Energetics of alloys

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### INTRODUCTION

Calculations on one-dimensional differential equations and simplified three-dimensional tight-binding models have proved helpful in the development of a theory for the electronic states of macroscopic solids that do not have translational symmetry.<sup>1</sup> Using modern order- $N$  methods, it is now possible to calculate the electronic states of large clusters of atoms with realistic self-consistent density functional theory local density approximation (DFT-LDA) potentials. It has been proposed by Anderson,<sup>2</sup> quite correctly, that certain aspects of the electronic structure of macroscopic solids must be qualitatively different from those of finite clusters of atoms, and this argument holds even if the clusters are periodically reproduced to fill all space. When coupled with other theoretical insights, however, results for large finite systems can be extrapolated to give a reliable picture of the electronic states of macroscopic disordered systems.

Perhaps the simplest system without long-range order is the disordered alloy, which can be modeled theoretically by distributing atoms on the sites of a Bravais lattice randomly with probabilities  $c$  and  $1-c$ , and can be fabricated experimentally by annealing certain metallic alloys at high temperature and then rapidly quenching them. An intermetallic compound, on the other hand, can be fabricated by annealing certain alloys that have a specific concentration for a long period of time at a temperature just below the ordering temperature. It is described theoretically as an ordered structure with a symmetry given by one of the tabulated space groups, and the compounds that have been identified have a relatively small number of atoms in the unit cell. Conceptually, it would be possible to create an ordered intermetallic compound by the statistical process described above, but the probability of obtaining one approaches zero rapidly as the number of atoms in the sample becomes large. For this reason, it is said that the random laying down of atoms on the sites produces a disordered alloy with probability one.

Certain properties of the disordered alloy are qualitatively different from the properties of an intermetallic compound. A simple example of a property that demonstrates this qualitative difference is the finite residual resistivity of the disordered alloy, which is the resistivity in the limit as the temperature approaches zero. An ordered intermetallic compound will have a resistivity at  $T=0$  that is essentially zero or infinity. A less simple example is Anderson localization.<sup>3</sup>

In the early days of alloy theory, Lifshitz argued on intuitive grounds that one can calculate the properties of a disordered alloy from one sufficiently large sample,<sup>4</sup> and referred to this property of a large sample as self-averaging. It can be seen most easily in exact

calculations of the electron or phonon density of states of finite one dimensional models of disordered alloys. It is observed in such calculations that the densities of states  $g(E)$  of two different random chains are indistinguishable when the chains are sufficiently long, provided the concentration  $c$  is the same for both samples. This is true even though  $g(E)$  is a very irregular function. It has been shown that the peaks that are seen in a calculation of  $g(E)$  on one energy mesh can be resolved into still narrower peaks when the mesh is made smaller, and, in fact, the function fluctuates at every scale.<sup>5</sup>

## FREE ENERGIES OF MIXING FROM DFT-LDA CALCULATIONS

In this paper, the electronic structure of disordered Cu-Zn alloys are studied by calculations on models with Cu and Zn atoms distributed randomly on the sites of fcc and bcc lattices. Concentrations of 10%, 25%, 50%, 75%, and 90% are used. The lattice spacings are the same for all the bcc models, 5.5 Bohr radii, and for all the fcc models, 6.9 Bohr radii. With these lattice constants, the atomic volumes of the atoms are essentially the same in the two different crystal structures. Most of the bcc models contain 432 atoms and the fcc models contain 500 atoms. These clusters are periodically reproduced to fill all space. Some of these calculations have been described previously.<sup>6</sup> The test that is used to demonstrate that these clusters are large enough to be self-averaging is to repeat selected calculations with models that have the same concentration but a completely different arrangement of Cu and Zn atoms. We found differences that are quite small, and will be specified below in the discussions of specific properties.

These calculations would have been impossible without a new order- $N$  method that is called the locally self-consistent multiple scattering (LSMS) method. A complete description of the LSMS is in the literature.<sup>7</sup> Briefly, when solving the multiple-scattering problem, the interaction of an atom with all neighbors out to seven or more nearest-neighbor shells is treated exactly. The interaction with the remaining infinity of atoms is treated approximately. This process is repeated for each of the  $N$  atoms in the cell, and the entire process is iterated until self-consistency is attained. The analytic properties of the single particle Green's function and the variational properties of the LDA are exploited, but the calculations would still be rather time consuming without a massively parallel supercomputer.

The free energy of mixing  $U_{\text{mix}}$  for the fcc Cu-Zn alloys is shown as a function of concentration in Fig. 1. It is obtained from the usual formula

$$U_{\text{mix}} = U_{\text{alloy}} - cU_{\text{Cu}} - (1-c)U_{\text{Zn}},$$

where the binding energy of the alloy  $U_{\text{alloy}}$  is obtained with the LSMS, and the binding energies of Cu and Zn are obtained from a consistent band theory calculation. The binding energy  $U_{\text{alloy}}$  was also calculated with two different versions of the coherent potential approximation (CPA).<sup>8</sup> The first one is called the self-consistent-field Korringa-Kohn-Rostoker CPA (SCF-KKR-CPA). In it, the DFT-LDA potentials are obtained using a prescription proposed some time ago.<sup>9</sup> The potentials for the second CPA are obtained by simply averaging the Cu and Zn potentials from the LSMS, and is called the CPA-LSMS. It can be seen that the curve corresponding to the SCF-KKR-CPA falls closer to the LSMS curve than does the one corresponding to the CPA-LSMS, although one would expect that the potential functions used in the latter version are better. However, the formulas used to evaluate  $U_{\text{alloy}}$  for both of these CPA's do not include the interatomic Coulomb energy. Adding the interatomic Coulomb energy  $U_C$ , which was calculated from the LSMS and discussed in previous publications,<sup>10</sup> it can be seen that the sum  $U_{\text{alloy}} + U_C$  agrees better with the LSMS values if  $U_{\text{alloy}}$  is calculated with the CPA-LSMS potentials. Of course,  $U_{\text{alloy}}$  calculated with the LSMS contains the interatomic Coulomb energy automatically.

It can be seen that both of the CPA's reproduce the concentration dependence of  $U_{\text{mix}}$  quite well, even though it is not a simple parabola. The fact that a cancellation of errors causes the SCF-KKR-CPA results to be quite near the LSMS ones may be one of the reasons that results obtained over the years with that approach have been quite acceptable. After the inclusion of the Coulomb bonding, the CPA-LSMS gives a  $U_{\text{mix}}$  that is surprisingly good considering other aspects of the approximation that will be illustrated below.

The concentration dependence of the average electron transfer from the Zn to the Cu atoms calculated with the LSMS, SCF-KKR-CPA, and CPA-LSMS are shown in Fig. 2. The values obtained with the CPA-LSMS are almost the same as those from the LSMS, but



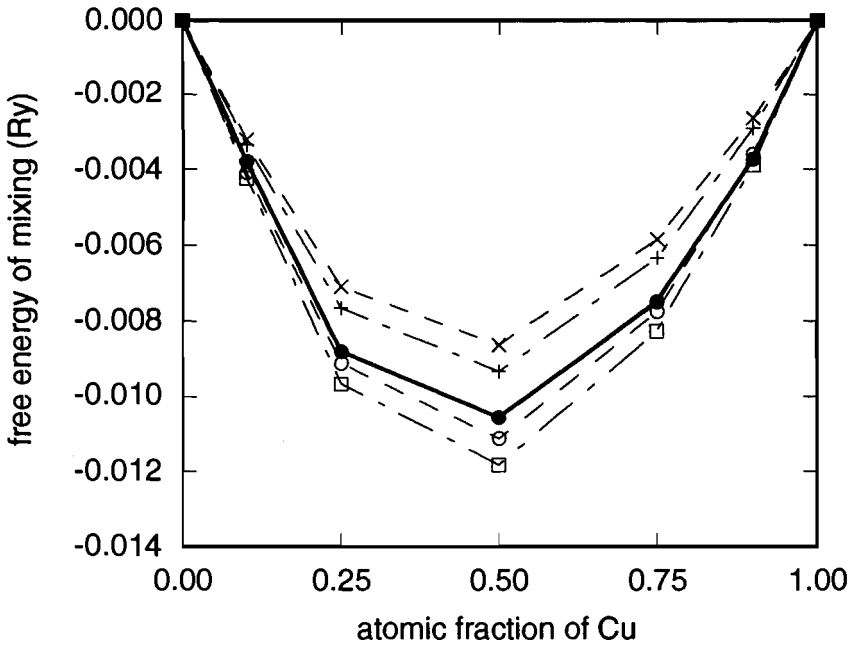


**Figure 1.** The free energies of mixing of fcc disordered alloys. The filled circles connected with a solid line are the energies calculated with the LSMS. The crosses connected with a dotted line are the energies calculated with the CPA-LSMS without the Coulomb energy, while the open circles connected with dotted lines include the Coulomb contribution. The pluses connected with a dashed-dotted line are the energies calculated with the SCF-KKR-CPA without the Coulomb energy, while the squares connected with dashed-dotted lines include the Coulomb contribution.

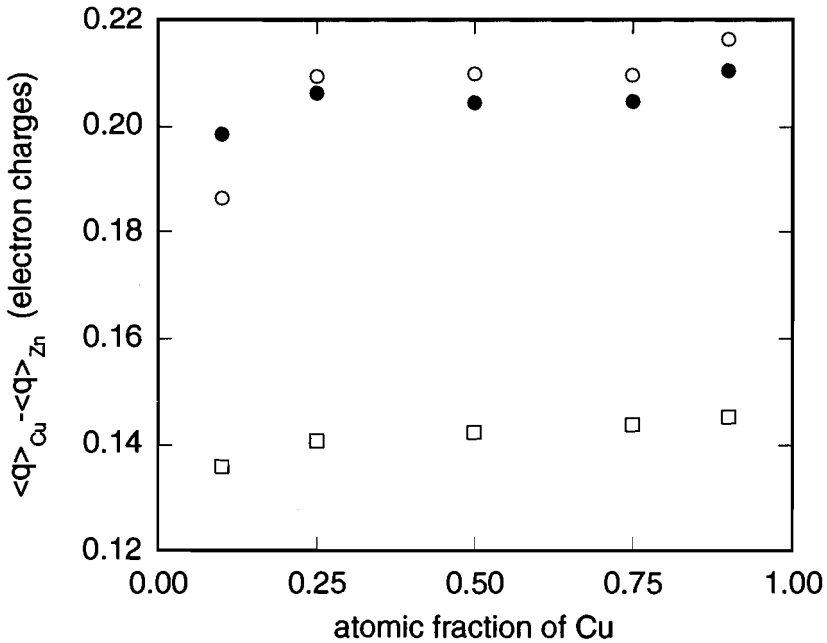


**Figure 2.** The average number of electron charges transferred from Zn atoms to Cu atoms in fcc disordered alloys. The solid dots are calculated with the LSMS. The open circles are obtained using the CPA-LSMS. The squares are obtained using the SCF-KKR-CPA.

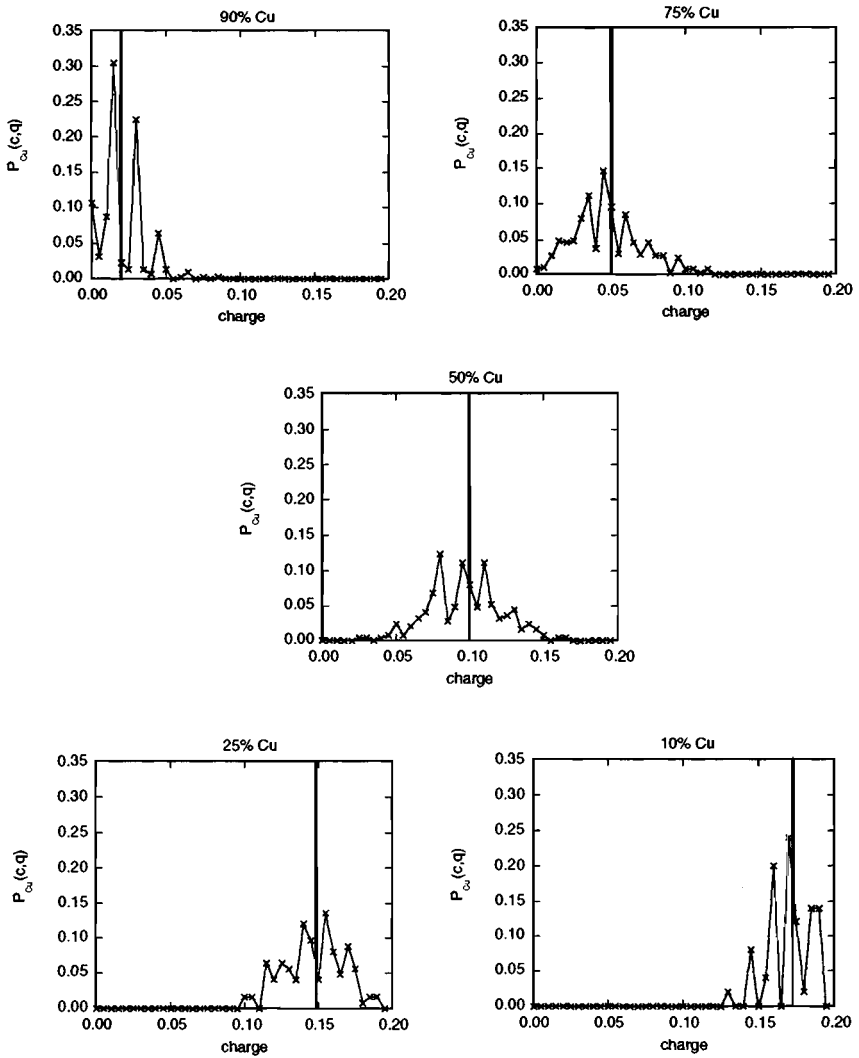


**Figure 3.** The probabilities for finding a charge between  $q$  and  $q+dq$  on a Cu atom for the five fcc disordered alloys. The average charge on the Cu sites is indicated by the heavy line.

the electron transfer from the SCF-KKR-CPA is only 2/3 of the correct value. In the light of this, it is even more surprising that the free energy of mixing calculated with the SCF-KKR-CPA is as good as it is.

The CPA is supposed to be a simple and inexpensive way to calculate the electronic structure of alloys, and it is not consistent with the philosophy to use a massive order- $N$  method like the LSMS to generate potentials for it. At the present time, no alternative method has been conclusively demonstrated to produce such good potentials. A method that has been suggested very recently seems very promising.<sup>11</sup> It provides a method for calculating both  $U_{\text{alloy}}$  and  $U_{\text{C}}$ .

## DISTRIBUTION OF CHARGES IN DISORDERED ALLOYS

The LSMS calculations produce a different charge for every Cu and Zn atom in the alloy, while the CPA is based on the approximation that every Cu atom has the average charge  $\langle q \rangle_{\text{Cu}}$  and every Zn atom has  $\langle q \rangle_{\text{Zn}}$ . The severity of this approximation can be illustrated by calculating from the LSMS data the probability  $P_{\text{Cu}}(c,q)$  that a Cu atom in an

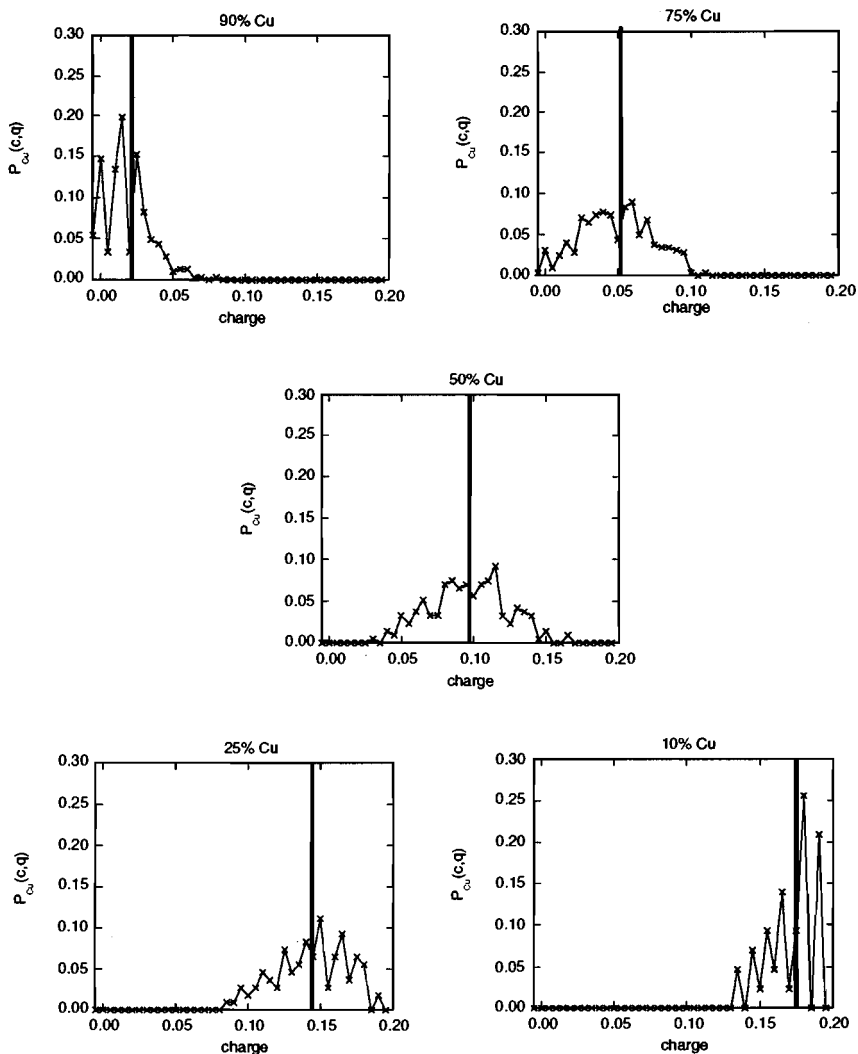


**Figure 4.** The probabilities for finding a charge between  $q$  and  $q+dq$  on a Cu atom for the five bcc disordered alloys. The average charge on the Cu sites is indicated by the heavy line.

alloy with a Cu concentration of  $c$  will have a charge between  $q$  and  $q+dq$ . These probability functions are shown in Fig. 3 for the fcc alloys with five concentrations. The value of  $dq$  is chosen to be 0.005 electron charges in all calculations. The averages  $\langle q \rangle_{Cu}$  are shown in those drawings by the heavy line. The same probability functions and  $\langle q \rangle_{Cu}$  are shown in Fig. 4 for the five bcc alloys. Given the breadth of the distribution of charges around the mean  $\langle q \rangle_{Cu}$ , it is surprising that the CPA has as much success as it does in describing certain properties of alloys.

The functions  $P_{Cu}(c,q)$  for the fcc alloys can be averaged over the concentration  $c$  to obtain a probability  $P_{Cu}(q)$  that a Cu atom in any fcc alloy will have a charge between  $q$  and  $q+dq$ . Recall that all of our calculations for fcc were carried out with the same lattice constant. We approximate this function by averaging over the five concentrations that we considered, giving equal weight to all of them. It can be seen from the plot of this function in Fig. 5 that the probability is not uniform in  $q$ , but has thirteen prominent peaks. Since there are twelve atoms on the nearest-neighbor (nn) shell in a fcc lattice, it is reasonable to write  $P_{Cu}(q)$  as the sum of conditional probabilities  $P_{Cu}(c_1,q)$  where  $c_1$  is the concentration of Cu atoms on the nn-shell. Five of the possible thirteen conditional probabilities are also plotted in

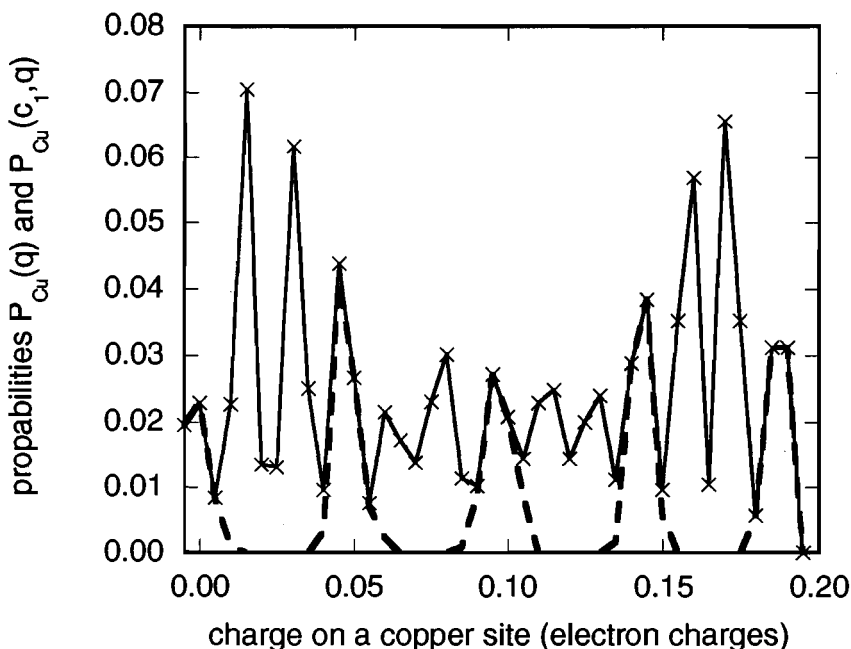


**Figure 5.** The solid line shows the probability for finding the charge on a Cu site between  $q$  and  $q+dq$  in a fcc disordered alloy with any concentration. The dotted lines show the conditional probabilities corresponding to sites with a concentration of Cu atoms on the nearest-neighbor shell of 100%, 75%, 50%, 25%, and 0%.

Fig. 5. The one that has non-zero values only near  $q=0.0$  corresponds to twelve Cu atoms on the nn-shell,  $c_1=100\%$ . It is known that an atom on a site surrounded by like atoms behaves somewhat like an atom in a pure crystal, and would have little net charge. The conditional probability centered near  $q=0.2$  corresponds to  $c_1=0\%$ , with all the neighboring atoms Zn. Such an atom behaves like a Cu impurity in a Zn crystal. The probabilities  $P_{Cu}(c_1, q)$  for  $c_1=25\%$ , 50%, and 75% have their centers between these limits. The conditional probabilities have a structure themselves. Extrapolating, it should be possible to write  $P_{Cu}(c_1, q)$  as a sum of the conditional probabilities  $P_{Cu}(c_1, c_2, q)$  where  $c_2$  is the concentration of Cu atoms on the second nn-shell. That probability could, in turn, be written as the sum of probabilities  $P_{Cu}(c_1, c_2, c_3, q)$ , where  $c_3$  is the concentration of Cu atoms on the third nn-shell.

It can be seen from Fig. 5 that knowledge of the concentration of atoms on the nn-shell severely restricts the possible charges that an atom on the site can have, although  $P_{Cu}(c_1, q)$  is clearly not a  $\delta$ -function as has been suggested.<sup>12</sup> Many more LSMS calculations would have to be done in order to determine the structure of  $P_{Cu}(c_1, q)$  for fcc alloys in detail, but it is easier to see the structure in the conditional probability for bcc alloys. The probability  $P_{Cu}(q)$  for finding a charge between  $q$  and  $q+dq$  on a Cu site in a bcc Cu-Zn alloy and three conditional probabilities  $P_{Cu}(c_1, q)$  are shown in Fig. 6. These functions were obtained, as for the fcc case, by averaging the LSMS data for the bcc alloys with five concentrations. The probability function is not a uniform function of  $q$ , but the structure is not as clear-cut as for the fcc case. The conditional probabilities  $P_{Cu}(c_1, q)$  are non-zero over a wider range than they are for the fcc alloys, and it can be seen clearly that they have fine structure as well. Presumably, each  $P_{Cu}(c_1, q)$  can be expressed as a sum of probabilities with two conditions  $P_{Cu}(c_1, c_2, q)$ , but there is no reason to expect even those probabilities to be  $\delta$ -functions.

In summary, the probability that a site will have a specific charge  $q$  is restricted to a very narrow range of values by specifying the composition of the first few nearest neighbor shells. Given the long-range nature of the Coulomb interaction, this may seem strange, but the environment of an atom is known to determine the density of states on the site which is related to the charge that the atom can sustain. At the same time, a knowledge of the concentration of any finite number of nn-shells will not specify the charge on a site exactly.

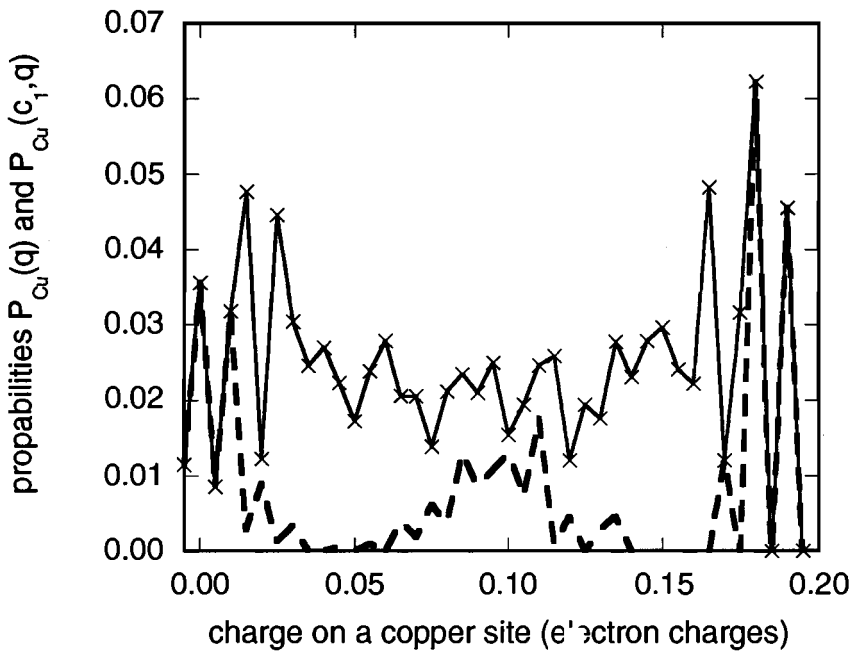


**Figure 6.** The solid line shows the probability for finding the charge on a Cu site between  $q$  and  $q+dq$  in a bcc disordered alloy with any concentration. The dotted lines show the conditional probabilities corresponding to sites with a concentration of Cu atoms on the nearest-neighbor shell of 100%, 50%, and 0%.

This can be described in terms of the Anderson proposition specialized for the present application, which states that certain properties of a macroscopic disordered alloy will be qualitatively different from those of an intermetallic compound. Specifically, the charges on a Cu or Zn atom in one of these alloys will take on a continuum of values. Once this is understood, it must be said that there will be applications in which it is a good approximation to replace one of the conditional probabilities  $P_{Cu}(c_1, q)$  with a  $\delta$ -function, or, as in the case of the CPA, to replace the probability  $P_{Cu}(c, q)$  illustrated in Figs. 3 and 4 with a  $\delta$ -function.

## THE $qV$ RELATION

It can be seen from Fig. 1 that, for some purposes, all of the Coulomb effects can be ignored, as has been done in the past. It might be concluded that too much time and effort was expended on this problem. On the other hand, it has been determined that an improvement on the SCF-KKR-CPA is worthwhile. In addition, a new correlation has been found from these numerical studies that is quite interesting in its own right.

Since the net charges on each site  $i$ ,  $q^i$ , are known from the LSMS, the Coulomb potential at the site can be calculated from the relation

$$V^i = \sum_{j=1}^N 2\alpha_{ij}q^j$$

where the sum is over the  $N$  atoms in the sample, and the matrix elements  $\alpha_{ij}$  are calculated by a technique that was derived by Ewald.<sup>13</sup> The  $\alpha_{ij}$  are defined so that they include the effect of the charges in all of the periodically reproduced cells. Thus, the sum is actually over an infinite number of charges. The  $V^i$  are plotted as a function of the net charges  $q^i$  in Fig. 7 for a model of a 50% copper-zinc alloy with the nuclei placed on the ideal lattice sites of a bcc crystal with a lattice constant of 5.5 Bohr radii. The number of atoms  $N$  in the cell for this calculation is 1 024, so there are 512  $q^i$ ,  $V^i$  points corresponding to copper sites and 512

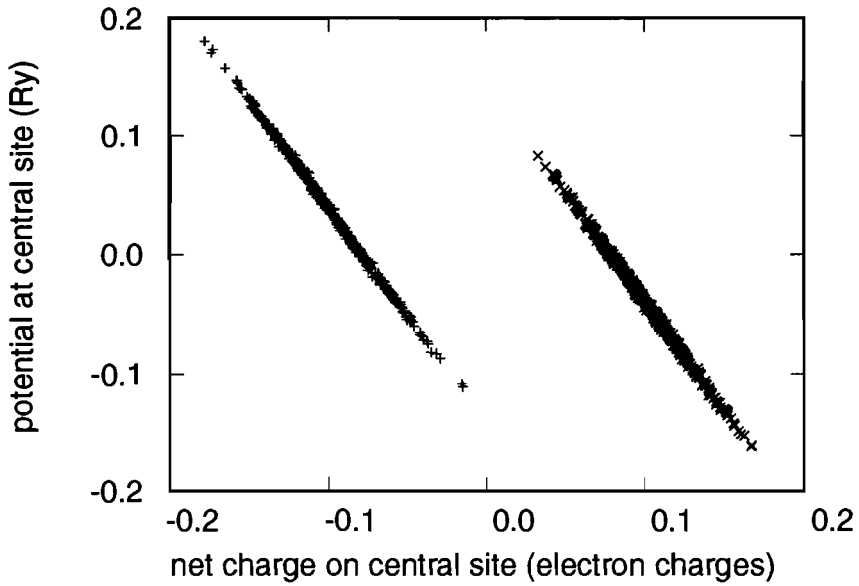


**Figure 7.** The Coulomb potential at a site plotted versus the net charge. The crosses are for the Cu sites and the plusses are for the Zn sites.

corresponding to zinc sites. The atoms were distributed on the sites with the help of a random number generator. The charges of the copper atoms are positive, which is consistent with the definitions stated above because the copper atoms gain electrons from the zinc atoms.

It can be seen from Fig. 7 that  $V^i$  is a linear function of the  $q^i$ . This  $qV$  relation was pointed out and discussed at some length in the papers in ref. 6. It is not simple electrostatics in that it would not exist for an arbitrary set of charges on the sites, even if the potentials are calculated exactly. The charges must be the result of a self-consistent LDA calculation. The linearity of the relation and the closeness of the points to the line is demonstrated by doing a least squares fit to the points. The sums that define the potentials  $V^i$  do not converge at all rapidly, as can be seen by calculating the Coulomb potential from the standard formula for one nn-shell after another. The  $qV$  relation leads to a special form for the interatomic Coulomb energy of the alloy

$$u_C^q = u_{C1} + u_{C2},$$

where

$$u_{C1} = \alpha \frac{1}{2} \langle q \rangle_{Cu} \langle q \rangle_{Zn},$$

and

$$u_{C2} = -\beta_{Cu} \frac{c}{2N_{Cu}} \sum_{i \in Cu}^{N_{Cu}} (q^i - \langle q \rangle_{Cu})^2 - \beta_{Zn} \frac{1-c}{2N_{Zn}} \sum_{i \in Zn}^{N_{Zn}} (q^i - \langle q \rangle_{Zn})^2.$$

The constants  $\beta_{Cu}$  and  $\beta_{Zn}$  are the slopes of the straight lines in Fig. 7, and  $\alpha$  is a constant that is roughly equal to two divided by the nn-shell radius.

Our best understanding to date of this  $qV$  relation is that it has the same origin in the DFT-LDA equations as the Harris energy approximation.<sup>14</sup> The concept that certain fragments retain their identity in total energy calculations that was demonstrated by Harris

appears in the above equations for  $u_C^q$ , where the fragments are the average Cu and Zn atoms. This  $qV$  relation can be used to define the contribution to the total energy due to a site if the charge on that site is known by any means, which can be a useful observation in approximate theories for alloys. It is not in conflict with the observations made above about the possible range of charges that a site can sustain have if it has a specified environment. It

provides a further evidence that the distribution of charges in a macroscopic disordered alloy must be continuous, since the qV relation is not consistent with a discrete set of charges.

## ACKNOWLEDGMENTS

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## CRYSTAL STRUCTURE AND PHASE STABILITY IN $\text{Fe}_{1-x}\text{Co}_x$ FROM AB INITIO THEORY

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The crystal structure for many metals is well established, and early research discovered a pattern which was shown to depend on the chemical periodicity of these elements. Particularly for the non-magnetic metals in the  $4d$  and  $5d$  transition metal series a connection between the atomic number and the crystal structure was recognized<sup>1</sup>. The crystal structure sequence involved more (fcc and hcp) or less (bcc) close-packed structures with high symmetry. The fact that the rare-earth elements show a regular behavior of the crystal structure as a function of atomic number led to the proposal<sup>2</sup> that the occupation of the  $d$  states was the important parameter for the crystal structure for these metals. This could then explain the more dramatic behavior of the  $d$  transition metals compared to the rare-earths since for the latter the occupation of the  $d$  states does not change much over the series whereas for the transition metals the  $d$  band is successively being filled when proceeding through the series.

The crystal structure for the magnetic  $3d$  transition elements shows, however, a different pattern governed by their magnetic properties. It was shown recently<sup>3</sup> that similar arguments as presented for the explanation of the crystal structure sequence for the non-magnetic metals could be applied also for the magnetic transition metals. Namely, by assuming saturated magnetism (one spin band being completely filled) and only study the remaining spin band, containing at most 5  $d$  electrons, one could use simple models<sup>4</sup> based on canonical band theory to understand the sequence bcc (Fe)  $\rightarrow$  hcp (Co)  $\rightarrow$  fcc (Ni). Also the equilibrium lattice parameter and the bulk modulus are anomalous for these magnetic metals compared to the non-magnetic ones. The lattice parameter is larger and the bulk modulus lower than expected for a non-magnetic transition metal. Again, these anomalous properties could be accounted for by assuming that one spin band is filled and does not contribute to the bonding and therefore only the  $d$  states of the other spin contributes. This weakens the chemical bond since only one spin band participate in the bonding and consequently the lattice parameter becomes larger and the bulk modulus lower.



In the present paper we focus on the alloys between Fe and Co. From the above discussion it is clear that the magnetic properties are very essential for these alloys. Since the occupation of the  $d$  states is the important parameter for most of the bulk properties for the  $d$  transition metals including their crystal structure we expect a phase diagram of  $\text{Fe}_{1-x}\text{Co}_x$  which depend largely on the spin-polarization. Although simple canonical band models would give a quantitative picture, we can not assume that it is accurate enough to describe the phase diagram of  $\text{Fe}_{1-x}\text{Co}_x$  qualitatively. Hence we have used a more elaborate method to calculate the spin moment and crystal structure energies which we intend to compare our canonical band results and experiments with.

We have used the multisublattice generalization of the coherent potential approximation (CPA) in conjunction with the Linear-Muffin-Tin-Orbital (LMTO) method in the atomic sphere approximation (ASA). The LMTO-ASA is based on the work of Andersen and co-workers<sup>5-8</sup> and the combined technique<sup>9,10</sup> allows us to treat all phases on equal footing. To treat itinerant magnetism we have employed for the local spin density approximation (LSDA) the Vosko-Wilk-Nusair parameterization<sup>11</sup>.

We have studied the fcc, bcc, and hcp (with ideal  $c/a$  ratio) phases as completely random alloys, while the  $\alpha'$  phase for off-stoichiometry compositions has been considered as a partially ordered alloy in the B2 structure with one sub-lattice (Fe for  $c < 50\%$  and Co for  $c > 50\%$ ) fully occupied by the atoms with largest concentration, and the other sub-lattice randomly occupied by the remaining atoms.

We note that the ground-state of iron is sensitive to approximations commonly used within density functional calculations. For instance, a local approximation for the exchange/correlation functional tend to underestimate the magnetic contribution to the total energy and therefore in certain calculations the non-magnetic fcc phase has wrongly been predicted as the ground-state of Fe<sup>12,13</sup>. However, the present calculations does not suffer from this problem and to check our calculations we have compared our ASA-LSDA calculations with highly accurate full potential calculations which include a gradient corrected approximation for the exchange/correlation functional (FP-GGA)<sup>14</sup>. We find very good agreement between those two methods as regards energy differences and magnetic moments. Both methods correctly predict magnetic bcc Fe as the ground-state and the transition pressure bcc  $\rightarrow$  hcp is in close agreement with each other and experiment ( $\sim 10$  GPa).

Let us turn to the results of our calculations. In Fig. 1 we show our full calculations using ASA-LSDA with the CPA for the  $\text{Fe}_{1-x}\text{Co}_x$  alloys. This is a two panel plot which in the upper panel (a) displays our calculated crystal structure energy differences with respect to the fcc structure energy, which defines the zero energy level. For the pure metals Fe and Co we show full potential results (FP-GGA) as a comparison. Solid circles refers to bcc-fcc energy differences and solid triangles to hcp-fcc energy differences. They are obviously in very good agreement with the ASA-LSDA-CPA results. Experimentally, at low temperatures, there are three phase transitions as a function of alloying,  $\alpha\text{-Fe}$  (bcc)  $\rightarrow \alpha'$  (B2)  $\rightarrow \epsilon\text{-Fe}$  (bcc)  $\rightarrow \epsilon\text{-Co}$  (hcp). Our calculations show the same behavior for the  $\text{Fe}_{1-x}\text{Co}_x$  alloys. In the second (b) panel of Fig. 1 our calculated mean magnetic moments are compared to experimental data<sup>15</sup>. Open circles (bcc), open squares (fcc) and open triangles (hcp) refers to the experimental data. The overall agreement between theory and experiment is impressive. For the bcc alloys we note that the magnetic moment is only weakly dependent on the actual alloying. It reaches a maximum value at about 30% of Co which compares well with previous studies<sup>3,16,17</sup>. Notice also that for the fcc and the hcp structures there are transitions from low-spin states to high-spin states, see Fig. 1 (b).

We would like to emphasize the great importance the magnetism have in the phase diagram of the Fe-Co alloys. For instance, paramagnetic calculations gives total energies for the bcc structure lying about 10-20 mRy higher than the fcc structure energy within the whole concentration range. The paramagnetic results (not shown) are more indicative for the behavior of the 4d alloys Ru-Rh or the 5d alloys Os-Ir.

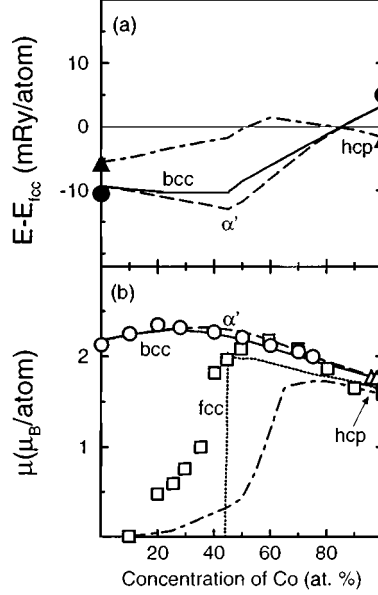


**Figure 1.** The energy of bcc and hcp random alloys and the partially ordered  $\alpha'$  phase relative to the energy of the fcc phase (a), of the Fe-Co alloy as a function of Co concentration. The corresponding mean magnetic moments are shown in (b). The ASA-LSDA-CPA results are shown as a dashed line for the  $\alpha'$  phase, as a full line for the bcc phase, as a dot-dashed line for the hcp phase, and as a dotted line for the fcc phase. The FP-GGA results for pure Fe and Co are shown in (a) by the filled circles (bcc-fcc) and triangles (hcp-fcc). In (b) experimental mean magnetic moments<sup>15</sup> are shown as open circles (bcc), open squares (fcc) and open triangles (hcp).

Next we turn to our canonical band results. To do so we have used a generalized canonical band model that includes spin-polarization. Hence we introduce a spin dependent shift,

$$\Delta_{ex} = \mu I_d, \quad (1)$$

to the LMTO canonical structure constant matrix for the  $d$ -states,  $S_{lm,lm'}$ ,

$$S_{lm\sigma,lm'\sigma'} = \begin{pmatrix} S_{lm,lm'} & 0 \\ 0 & S_{lm,lm'} \end{pmatrix} + \begin{pmatrix} -\delta_{m,m'}\Delta_{ex}/2 & 0 \\ 0 & +\delta_{m,m'}\Delta_{ex}/2 \end{pmatrix}. \quad (2)$$

Using this model in analogy with previous studies<sup>18</sup> we can calculate a magnetic moment ( $\mu$ ) of the system with fixed Stoner exchange parameter  $I_d$  and occupation of the  $d$  states. The total energy could then be calculated as the balance between the kinetic energy and the spin-polarization energy:

$$E_{tot} = \langle T \rangle - \mu^2 I_d / 4. \quad (3)$$

The Stoner exchange parameter was chosen so that the magnetic moment behaved similarly to the magnetic moment for the real Fe-Co alloy. These values were, however,

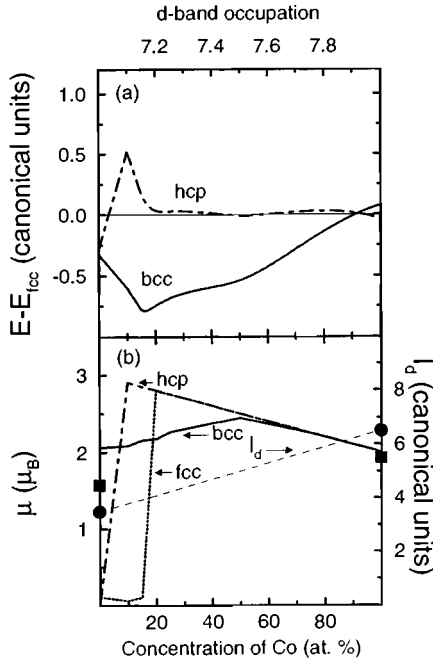


**Figure 2.** The structural energy difference (a) and the magnetic moment (b) as a function of the occupation of the canonical  $d$ -band  $n$  corresponding to the Fe-Co alloy. The same lines as in Fig. 1 are used for the different structures. In (b) the concentration dependence of the Stoner exchange integral  $I_d$  used for the spin-polarized canonical  $d$ -band model calculations is shown as a thin dashed line with the solid circles. The value of  $I_d$  for pure Fe and Co, calculated from LSDA and scaled to canonical units, are also shown in (b) as solid squares.

close to the calculated (LSDA) correspondence. It is interesting to note in Fig. 2 that the calculated crystal structure energy differences agree fairly well with those calculated from the ASA-LSDA-CPA method. To a large extent this agreement can be understood from the fact that Fe and Co are neighboring atoms in the Periodic Table. The alloy electronic structure exhibits an almost common band behavior for the spin up band, while a split band behavior, due to large difference in magnetic moments on the Fe and Co sites, occurs for the spin down band<sup>3,16,17</sup> However, this split band behavior is more pronounced for states above the Fermi energy, and consequently affects the total energy to a smaller degree.

In summary, we have demonstrated the possibility of calculating the phase stability of a magnetic random alloy from first principles by means of LMTO-CPA theory. Our calculated phase diagram is in good agreement with experiment and shows a transition from the partially ordered  $\alpha'$  phase to an hcp random alloy at  $\sim 85\%$  Co concentration.

We have also shown that the structural and phase stability in the Fe-Co alloy is induced by magnetism and have pointed out that it can be understood from the fractional filling of the polarized, minority spin  $d$ -band. Likewise, the magnetic properties are demonstrated to be determined by the atomic arrangement. That is the bcc phase has a stable magnetic moment in the complete concentration range, while the fcc and the hcp phases show high spin - low spin magnetic phase transitions.

We observe that for the Fe-Co system a simple spin polarized canonical model is able to reproduce qualitatively the results obtained by LMTO-CPA calculations. Despite the simplicity of this model the structural properties of the Fe-Co alloy are explained from simple band-filling arguments.

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# AB INITIO STUDY OF PHASE STABILITY AND EQUATION OF STATE OF TITANIUM DIOXIDE

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## INTRODUCTION

Titanium dioxide exists in nature as three different polymorphs: rutile, anatase and brookite. This material has been extensively studied during the last few decades due to its interesting physical properties and numerous technological applications. Rutile and anatase (a popular white pigment) are widely used in photocatalysis and as sensors. Both of them have had new structural and electronic applications suggested recently (see <sup>1</sup> for a review).

Numerous theoretical and experimental studies have dealt with the properties of rutile (see <sup>1-3</sup> and references therein), while the other polymorphs have attracted less attention. This is due to the fact that rutile is easier to grow and characterize, and has a simpler structure that can be readily investigated using a variety of theoretical techniques. The fact that the experimentally reported bulk modulus of anatase is in the range from 59 GPa <sup>4</sup> to 360 GPa <sup>5</sup> illustrates the need for further studies of titanium dioxide polymorphs.

Pressure-induced phase transitions in the titanium dioxide system provide an understanding of crystal structure and mineral stability in planets interior and thus are of major geophysical interest. Moderate pressures transform either of the three stable polymorphs into the  $\alpha$ -PbO<sub>2</sub> (columbite)-type structure, while further pressure increase creates the monoclinic baddeleyite-type structure. Recent high-pressure studies <sup>6-8</sup> indicate that columbite can be formed only within a limited range of pressures/temperatures, although it is a metastable phase that can be preserved unchanged for years after pressure release <sup>9</sup>. Combined Raman spectroscopy and X-ray diffraction studies <sup>6-8,10</sup> have established that rutile transforms to columbite structure at 10 GPa, while anatase and brookite transform to columbite at approximately 4-5 GPa.

The room temperature transformation of the columbite phase to baddeleyite commences at 13-17 GPa <sup>6</sup>, with transition pressure increasing linearly with temperature <sup>7</sup>. Direct transition from rutile to baddeleyite phase at room temperature and 12 GPa has also been reported <sup>7</sup>. The baddeleyite phase undergoes further transition to an as yet undefined high-symmetry structure at 70-80 GPa. The most likely candidate for the high-pressure phase is fluorite, which is consistent with the general pattern of increasing Ti coordination number from 6 in rutile, to 7 in baddeleyite (a distorted fluorite structure), and to 8 in fluorite.

This rich phase diagram has not yet been studied theoretically. The main challenge is to achieve the accuracy necessary for quantitative predictions. The energy difference between anatase and rutile is known to be small (0.05 eV/mol <sup>11</sup>), and other phases are relatively close in energy as is implied by the sluggish nature of all observed transitions. The accuracy sought in calculating energy differences between polymorphs requires high convergence of ab initio calculations and makes the problem computationally demanding.

It is important to apply a first principles technique since an alternative ionic modelling approach based on the Kim-Gordon formalism yields errors in the cell parameters as high as

6% and Ti-O bond lengths are in error by about 3% in all three stable polymorphs. Even the exact nature of the distortion of the Ti-O octahedra in rutile is described incorrectly<sup>12</sup>.

The detailed first principles study of the three stable polymorphs has been performed recently using the LCAO technique<sup>1</sup>. The main drawback of that work is that no cell optimization was performed for anatase or brookite. The energy-volume curves that were used to calculate the bulk modulus,  $B$ , and its pressure derivative,  $B'$ , have been produced by varying the volume with the  $c/a$  ratio and fractional atomic coordinates being fixed at experimental values which makes results unreliable.

This paper presents the results of *ab initio* calculation investigating the pressure dependence of properties of rutile, anatase and brookite, as well as of columbite and hydrothermal fluorite phases. The main emphasis is on lattice properties since it was possible to locate transitions and investigate transformation precursors by using constant-pressure optimization algorithm.

## COMPUTATIONAL TECHNIQUE

The pseudopotential density-functional technique is used to calculate total energies, forces on atoms and stress tensors as described in Ref. 13 and implemented in the computer code CASTEP. CASTEP uses a plane-wave basis set to expand wave-functions and a preconditioned conjugate gradient scheme to solve the density-functional theory (DFT) equations iteratively. Brillouin zone integration is carried out via the special points scheme by Monkhorst and Pack.<sup>14</sup> The nonlocal pseudopotentials in Kleyman-Bylander form were optimized in order to achieve the best convergence with respect to the basis set size.<sup>15</sup>

The main advantage of the plane wave basis set is that convergence can be easily achieved by increasing the energy cut-off for plane waves. The quality of Brillouin zone sampling can also be improved systematically by going to higher order sets of Monkhorst-Pack points. The convergence of 0.01 eV/mol and better is achieved for all the structures under study when using 900 eV energy cut-off and  $k$ -points with a spacing in the order of  $0.05 \text{ \AA}^{-1}$ . This corresponded to 10000 plane functions for brookite (24 atoms per cell), to 4000 functions for rutile (6 atoms per cell), and to approximately 7000 functions for calculations for other structures (12 atoms per cell).

Geometry optimization was performed using BFGS scheme for the Hessian update<sup>16</sup>, with cell variables and cartesian atomic coordinates treated on an equal footing. A typical optimization run to convergence (RMS force less than  $0.05 \text{ eV/\AA}$ , RMS stress less than  $0.1 \text{ GPa}$ ) required between 10 and 20 steps. It was important to apply the finite basis set correction<sup>17</sup> even for well converged calculations. This correction to stress, typically around  $0.1 \text{ GPa}$ , was needed to guarantee stability of the geometry optimization process.

Calculations for rutile and anatase were performed using both LDA level of DFT and the gradient corrected form of the exchange-correlation potential (GGA). The GGA approach is implemented self-consistently as described in<sup>18</sup> and not as a post-SCF correction.

## RESULTS AND DISCUSSION

Present in the next sections are the LDA results for equilibrium structure, pressure-induced transitions and electronic properties of various polymorphs, and the comparative analysis of the results for rutile and anatase that were obtained using LDA and GGA forms of the exchange-correlation potential.

### Ground State Properties of Titanium Dioxide Polymorphs

The energy minimization was applied to the space groups of the observed structures:  $P4/mnm$ ,  $I4_1/amd$ ,  $Pcab$ ,  $Pbcn$ ,  $P2_1/c$ , and  $Fm3m$  for rutile, anatase, brookite, columbite, baddeleyite and fluorite phases, respectively. The calculated ground state properties for the first four polymorphs are compared with experiment in Table 1, and the respective energy-volume curves are shown in Figure 1. Bulk moduli and their pressure derivatives presented in Table 1 were calculated by fitting the Birch equation of state to the curves in Figure 1.

These results show that the LDA description of equilibrium structures of all polymorphs gives good agreement with experimental data. The anatase-rutile energy difference is

predicted to be 0.033 eV/mol compared to the experimental value of 0.05 eV/mol <sup>11</sup> (ionic model gives 0.004 eV/mol <sup>12</sup>). Brookite in this calculation is less stable than rutile by 0.058 eV/mol (0.21 eV/mol in <sup>12</sup>).

**Table 1.** Calculated properties of rutile, anatase, brookite, and columbite phases. Relative deviation from experimental values is shown in brackets. Structural experimental data are from 19,20,21,9 respectively. Bulk modulus of rutile extrapolated to 0 K is from <sup>2</sup>.

|                                   | Rutile         | Anatase        | Brookite          | Columbite      |
|-----------------------------------|----------------|----------------|-------------------|----------------|
| Volume (Å <sup>3</sup> /mol)      | 31.535 (+1%)   | 35.009 (+1.5%) | 32.611 (+1.4%)    | 30.855 (+0.7%) |
| a (Å)                             | 4.6033 (+0.2%) | 3.7814 (-0.1%) | 9.2006 (+0.2%)    | 4.5689(+0.1%)  |
| b (Å)                             | –              | –              | 5.4640 (+0.3%)    | 5.4806 (+0.2%) |
| c (Å)                             | 2.9763 (+0.6%) | 9.7929 (+2%)   | 5.1896 (+0.9%)    | 4.9288 (+0.4%) |
| c/a                               | 0.647 (+0.4%)  | 2.590 (+3%)    |                   |                |
| ξ (y <sub>Ti</sub> for columbite) | 0.3039 (-0.3%) | 0.2035 (-1.5%) |                   | 0.174 (+2%)    |
| Ti-O distances (Å)                | 1.978 (0.1%)   | 1.993 (0.5%)   | 1.95-2.02 (1-3 %) | 2.046 (0.2%)   |
|                                   | 1.961 (0.5%)   | 1.945 (0.8%)   |                   | 1.958 (0.9%)   |
|                                   |                |                |                   | 1.916 (0.8%)   |
| B (GPa)                           | 244 (+2%)      | 190            | 220               | 215            |
| B'                                | 5.4 (-20%)     | 4.3            | 3.9               | 4.5            |

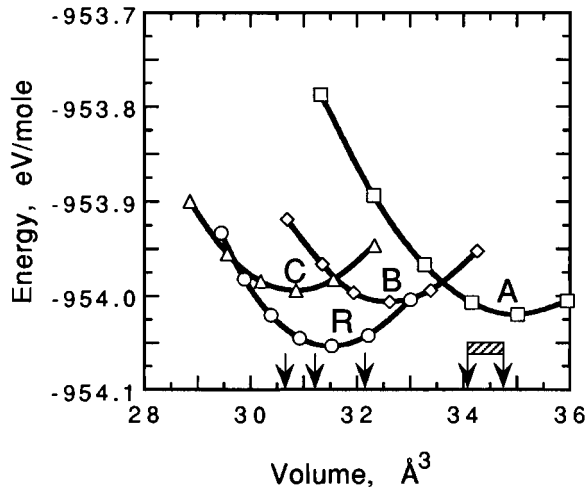


**Figure 1.** Volume dependence of the total energy of rutile (R), anatase (A), brookite (B) and columbite (C) phases. Experimental values of the unit cell volume at ambient conditions are shown with arrows in the following order: C-R-B-A (experimental scatter for anatase is illustrated with a box).

### Pressure Induced Phase Transformations

Transition pressures were determined by equating enthalpies of different polymorphs via the common tangent construction. We found that rutile transforms to columbite structure at 11.8 GPa with a small volume change of 3%. These results agree well with experimental

observations<sup>6-8</sup>. Transition pressure for the anatase  $\rightarrow$  columbite transformation is much smaller (1.2 GPa) and the associated volume change of 11% is bigger. Experimental values are 4.5 GPa and 8%, the discrepancy being consistent with the fact that the calculated equilibrium volume is higher than the measured one. There is also a substantial scatter in experimental data for anatase, as illustrated in Figure 1.

Transformation from brookite to columbite is predicted to occur at 2 GPa with a 2% volume change; no directly comparable experimental data are available.

Preliminary results for baddeleyite phase indicate that it is very close in energy to columbite but at  $P=0$  its volume is 8% smaller than that of the columbite structure. The predicted structure for this monoclinic phase at 0 GPa is:  $a=4.7901$  Å,  $b=4.9151$  Å,  $c=4.9241$  Å,  $\beta=99.968^\circ$ ,  $V=28.546$  Å<sup>3</sup>/mol, Ti (0.2793, 0.0472, 0.2085), O1 (0.0783, 0.3535, 0.3293), O2 (0.4439, 0.7610, 0.4845).

The fluorite phase is found to be extremely high in energy (it falls outside the energy range of Figure 1). Its equilibrium volume at  $P=0$  would be 27.648 Å<sup>3</sup>/mol, and calculated equation of state gives  $B=287$  GPa and  $B'=4.18$ . These values make fluorite structure the least compressible of all titanium dioxide polymorphs studied here, but still leaves the observation of a phase with  $B>500$  GPa unexplained.<sup>4</sup>

The main problem related to the use of pseudopotentials in studies of solids under pressure is to make sure that the overlap of ionic cores does not increase significantly when interatomic distances decrease. The present study is certainly not affected by this potential pitfall since Ti-O distances typically change by no more than 0.1 Å over the pressure range investigated. However, theoretical studies of fluorite and related phases at pressures of around 100 GPa should be performed with added caution.

Finally, the use of the constant pressure minimization algorithm allows searching for phenomena that can be considered as precursors of pressure-induced transitions. For example, the predicted behaviour of the anatase cell constants as a function of pressure shows that the  $a(P)$  and  $c(P)$  plots are only linear for  $P<4$  GPa, the value that is close to both the theoretical and experimental transition pressures. At higher pressures the  $a$  constant starts to grow under compression, indicating inherent structural instability. In the case of rutile there is a different precursor effect, namely at 11 GPa the distances between the titanium atom and the two different oxygens, axial and equatorial, become equal. Once again, the pressure corresponds closely to the phase transition point.

## Comparison of LDA and GGA Exchange-Correlation Functionals

It is well established that GGA gives a better description of molecular systems, crystal surfaces and surface-molecule interactions. However, there are cases where the GGA results for solids are in much worse agreement with experiment than the LDA ones (e.g.,<sup>3,22</sup>). It has been suggested that the effect of using GGA for solids is roughly equivalent to adding uniform tensile stress, and as a result lattice constants are frequently overestimated.

**Table 2.** Ground state geometry of rutile.

|                          | $a$ (Å) | $c$ (Å) | $c/a$ | $\xi$  |
|--------------------------|---------|---------|-------|--------|
| LDA <sup>3</sup>         | 4.625   | 2.911   | 0.629 | 0.3050 |
| GGA <sup>3</sup>         | 4.781   | 3.072   | 0.643 | 0.3050 |
| LDA [present]            | 4.603   | 2.976   | 0.647 | 0.3039 |
| GGA [present]            | 4.624   | 2.992   | 0.647 | 0.3050 |
| experiment <sup>19</sup> | 4.594   | 2.958   | 0.643 | 0.3048 |

Table 2 shows that in the case of rutile the GGA overestimation of lattice constants is less important in the present calculation than in Ref. 3. Most likely explanation is that the GGA functional is used here only for solid state calculations and not for the pseudopotential generation from the free atom. This procedure has been shown to give more accurate structural results than with the GGA applied both in the potential generation and solid state



calculations. Likewise, it improves the accuracy of the total energies compared to the LDA results.<sup>3</sup> The first part of this statement is illustrated by Table 2: the current GGA data are closer to the LDA results, and to the experiment, than the consistently applied GGA ones.<sup>3</sup>

However, the unusual feature of the present results is that the use of GGA completely changes the topology of the phase diagram. Rutile becomes 0.06 eV/mol higher in energy than anatase which is in disagreement with experiment. This finding contradicts the common belief in advantages of GGA over LDA for study of energetics, even though it is accepted that often LDA is more accurate for structure determination. Apparently it is necessary to use nonlocal functionals to describe surfaces and molecules but caution should be exercised when applying this approach to bulk solids. The most likely explanation is that the gradient corrected functionals improve greatly over LDA in the spatial areas where the tails of charge density distribution are important. This is related to the well-known failure of LDA to reproduce the asymptotics of the exchange-correlation potential in atoms and on surfaces. Then GGA should not be expected to be particularly useful for bulk studies except for porous zeolite-like structures with internal surfaces.

## Electron Density of States

Calculated valence band (VB) densities of states (DOS) for all six polymorphs studied are presented in Figure 2. These plots correspond to zero pressure geometries.

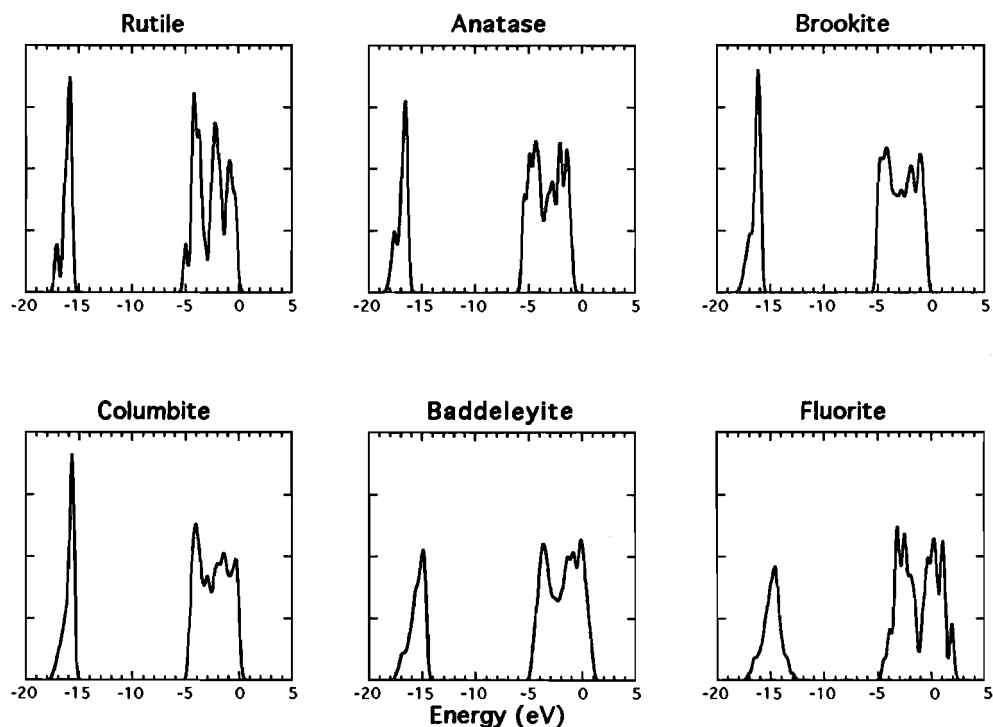


**Figure 2.** Density of electron states (states/eV) for six different polymorphs at  $P=0$ .

The upper VB for rutile is composed of the  $O_{2p}$  orbitals and is 5.52 eV wide. The lower  $O_{2s}$  band has a width of 2.08 eV. These numbers agree well with the experimental values of 5.4 and 1.9 eV, respectively.<sup>1</sup> The calculated direct energy gap of 1.83 eV is in good agreement with other LDA results and is smaller than the experimental value of 3.0 eV.<sup>1</sup>

The width of the upper VB in anatase is 5.12 eV, which is smaller than in rutile and is close to the experimental value of 4.75 eV.<sup>1</sup> The separation between the two major features of the upper VB is 2.3 eV compared to the measured 2.0 eV.<sup>1</sup> The lower VB is 2.05 eV wide, slightly wider than in rutile. Lower and upper VBs in brookite have a width of 2.20

and 5.13 eV, respectively, very close to those of anatase and to the LCAO calculation results (1.85 and 5.31 eV, respectively<sup>1</sup>).

High pressure polymorphs are naturally characterized by wider bands with a smaller gap between the upper and lower VBs. The upper VB width in columbite, baddeleyite and fluorite structures is 5.37 eV, 6.22 eV and 7.44 eV, respectively, while the lower VB width is 2.32 eV, 3.30 eV and 4.60 eV, respectively. This trend is due to the increasing overlap between the 2s-states of oxygen under compression.

## CONCLUSIONS

It has been shown that ab initio total energy DFT approach is a suitable tool for studies of phase equilibria at low temperatures and high pressures even when small energy differences of the order of 0.01 eV/mol are involved. The constant pressure optimization algorithm that has been developed here allows for the calculation of the equation of state for complex structures and for the study of precursor effects related to phase transitions.

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## AUGMENTED SPACE RECURSION APPROACH FOR ALLOY PHASE STABILITY

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### INTRODUCTION.

One of the major ingredient for the understanding of alloy phase stability is the configurational energy. Models have been proposed to represent the configurational energies in terms of effective multisite interactions, in particular effective pair interactions (EPIs).

We have recently developed a scheme for calculating these EPIs based on the method of the augmented space recursion (ASR)<sup>1</sup> coupled with the orbital peeling technique<sup>2</sup> within the framework of the tight-binding linearized muffin-tin orbital (TB-LMTO) method<sup>3</sup> for the description of the electronic structure. Our scheme of calculation is similar to other methods based on embedding clusters in an effective medium<sup>4,5</sup>. The calculation involves the description of the electronic structure of components as well as averaging over different configurations of the system. It is precisely in this averaging scheme that methods based on the embedding cluster method (ECM) differ from one other. In the coherent potential approximation of the ECM (CPA-ECM)<sup>4</sup> the averaging is done within the framework of the CPA. In the direct configuration averaging (DCA)<sup>5</sup> the averaging is done directly by summing over different random configurations. In our scheme we employ the ASR for carrying out the configuration averaging. The CPA being a single-site approximation has its own limitations; on the other hand, in the DCA since the averaging is done by brute force method, in principle such a method cannot sample all possible realizations. Further the DCA method in the grand canonical scheme is not a justified method as discussed in details by Gonis *et. al* in ref(6).

The ASR provides an alternative means for configuration averaging which is not

restricted by the above limitations. The main advantage of the method is that it can take into account inhomogeneous disorder such as effects of clustering<sup>1</sup>, short-range order<sup>7</sup> and lattice relaxation<sup>8</sup>. Furthermore as the ASR is based on the recursion method, it can be applied to surfaces<sup>9</sup> without further extension.

The aim of the present communication is to apply the ASR-orbital peeling method for the study of phase ordering in PdV alloys and phase segregation in PdRh alloys.

## DETERMINATION OF EFFECTIVE PAIR INTERACTION

Often the most important effective cluster interaction of the concentration fluctuation expansion of the configurational free energy is the EPI which is defined as

$$E_{ij}^{(2)} = 1/4(V_{AA} + V_{BB} - V_{AB} - V_{BA}) \quad (1)$$

where  $V_{IJ}$  is the average energy of the disordered alloy with atomic species I and J at sites i and j, respectively. It gives the interchange energy associated with two sites embedded in an otherwise average medium, being occupied by A or B type of atom.

In the Hartree-Fock approximation, the total energy of a solid consists of two terms, an one electron band structure contribution  $V_{BS}$  and an electrostatic term  $V_{ES}$  which includes contributions from the coulomb repulsion of the ions and the correction for double counting the electron-electron and the exchange and correlation energy in  $V_{BS}$ . It is usually assumed that for energy differences like in eq. (1), the electrostatic contributions approximately cancel out and one is left with solely the one-electron band-structure term. This assumption is expected to be valid for alloys considered in the present communication. However for alloys with large charge transfer like Al-Li or Ni-Ti one need to go beyond this approximation. Considering only the band energy contribution, the EPI can be expressed in a convenient form in terms of a generalized phase shift  $h(E)$  as:

$$E_{ij}^{(2)} = - \int_{-\infty}^{E_F} h(E) dE$$

with

$$h(E) = 1/\pi \text{Im} \log \frac{\det < G_{AA} > \det < G_{BB} >}{\det < G_{AB} > \det < G_{BA} >}$$

where  $< G_{IJ} >$  refers to the configuration averaged Green function with averaging over all sites except in positions i and j, occupied by I and J atoms.

The operation involved in the definition of the EPI is an exchange of atoms on sites i and j and it is a kind of localized perturbation. So the orbital peeling method<sup>2</sup> provides an efficient means for obtaining the generalized phase shifts.

Without going into details we shall quote the final result of the orbital peeling method which expresses the EPI as a sum of terms involving the zeroes and the poles of peeled Green functions  $\langle \bar{G}_{IJ,k} \rangle$  ( $\langle \bar{G}_{IJ,k} \rangle$  denotes IJ block of the Green function corresponding to the Hamiltonian, where two atoms I and J are embedded at sites i and j and the orbitals from 1 to (k-1) are deleted at the site i.) :

$$2 \left( \sum_{\gamma} Z_{\gamma} - \sum_{\gamma} P_{\gamma} + (N_P - N_Z) E_F \right)$$

where  $N_P$  ( $N_Z$ ) is the number of poles (zeroes) below the fermi energy  $E_F$ . The factor 2 accounts for the spin degeneracy.

Table 1: Effective Pair Potentials in mRyd/atom for various distances between the pairs for a 50-50 PdV alloy. KKR-CPA-GPM values are taken from ref(10).

| PAIR INT.      | KKR-CPA-GPM | TBLMTO-ASR |
|----------------|-------------|------------|
| V <sub>1</sub> | 2.0         | 4.3        |
| V <sub>2</sub> | -0.8        | -0.1       |
| V <sub>3</sub> | 0.5         | 0.1        |
| V <sub>4</sub> | 0.1         | -0.2       |

We employ the ASR coupled with TB-LMTO for a first-principle determination of the configuration averaged peeled off Green function  $\langle \hat{G}_{IJ,k} \rangle = \langle (zI - H_k^{IJ})^{-1} \rangle$ .  $H_k^{IJ}$ , in the most localized sparse tight-binding representation of LMTO theory has both diagonal and off diagonal disorder. We retain this form of Hamiltonian and use the ASR for the calculation of the averaged Green function. The ASR has been discussed in great detail in earlier work<sup>1</sup> and we shall indicate here only its salient points. In the ASR one defines an effective, non-random Hamiltonian in augmented space and performs recursion with this effective augmented space Hamiltonian in order to get the continued fraction coefficients of the configuration averaged Green functions. For the purpose of calculating EPIs we obtain the continued fraction expansion coefficients of the configuration averaged Green functions for four possible occupancies of i and j, AA, AB, BA, BB, in each case the orbitals from 1 to 9 being peeled off one after another. The poles and zeros of these Green functions are obtained from computed L sets of continued fraction expansion coefficients. The poles and the zeros being the eigenvalues of the symmetric tridiagonal matrices of rank L and L-1 are obtained by the method of bisection based on the Sturm sequence property followed by Newton's method for isolated roots.

## PHASE ORDERING IN PdV ALLOYS

The stability properties of the Pd-V system is well studied both experimentally as well as by theoretical methods. Being a well studied alloy, we have results available for comparison so that the reliability of our methodology can be demonstrated.

In Figure 1(a) we plot the nearest neighbor EPIs as functions of energy at three different concentrations for the Pd-V alloy. The shape of the curves is in agreement with those obtained by other methodologies consisting of a phase separating region near the band edges and an ordering region near the center.

In table 1 we present the results for the EPIs up to the fourth nearest neighbors obtained from the KKR-CPA coupled with the generalized perturbation method(GPM)<sup>10</sup> along with our calculation for 50-50 PdV alloy<sup>1</sup>.

From the table we find some mismatch between the KKR-CPA-GPM and the present work for the numerical values of different EPIs. The reason may be attributed to the differences in the description of the electronic structure and in the averaging scheme involved in the two methodologies. The sign of  $V_4$  in our work is opposite to that of the KKR-CPA-GPM. However a negative sign of  $V_4$  is in agreement with work of Singh and Gonis<sup>11</sup> where they obtained a negative value of  $V_4$  within the frame-work of the KKR-ASA-CPA-GPM.

<sup>1</sup> $V_n = E_{ij}^2$ , j being the n-th nighbor of i

Table 2: Effective Pair Potentials in mRyd/atom for various distances between the pairs for a 50-50 PdRh alloy. KKR-CPA-GPM values are taken from ref(10).

| PAIR INT. | KKR-CPA-GPM | TBLMTO-ASR  |
|-----------|-------------|-------------|
| $V_1$     | -0.85       | -0.80       |
| $V_2$     | - 0.05      | -0.02       |
| $V_3$     | -0.12       | 0.1         |
| $V_4$     | $\approx 0$ | $\approx 0$ |

For the phase stability analysis we follow the method given by Kanamori and Kakehashi<sup>12</sup> of geometrical inequalities and compute the antiphase boundary energy defined by

$$\xi = V_2 - 4V_3 + 4V_4$$

The authors proved rigorously that for  $A_xB_{1-x}$  alloys with  $x$  confined to the range  $\leq 0.5$ ,  $DO_{22}$  structure and  $A_2B_2$  structure are the corresponding structures at  $x = 0.25$  and  $x = 0.5$  for  $\xi > 0$  and  $L1_2$  and  $L1_0$  are the corresponding ones at  $x = 0.25$  and  $x = 0.5$  for  $\xi < 0$ .

In Figure 1(b) we have plotted the negative of anti-phase boundary energy  $\epsilon = -\xi$  as a function of band filling for  $Pd_xV_{1-x}$  with  $x = 0.25, 0.5$  and  $0.75$ . The number of zeros is in agreement with the arguments based on moments (there has to be at least four zeros)<sup>13</sup>.

We find from Figure 1(b) that  $\epsilon < 0$  at  $E = E_F$  for  $x = 0.75$  suggesting that at this concentration  $DO_{22}$  structure is stable. A similar analysis shows that  $\epsilon > 0$  for  $x = 0.25$  at  $E = E_F$  and here the  $L1_2$  structure is stable. This is further supported by the fact that an exchange of stability between  $L1_2$  and  $DO_{22}$  occurs for large electron number. For  $x = 0.5$ , among the possible ground state configurations which are  $L1_0$  and  $A_2B_2$ , we find  $L1_0$  to be the stable one with  $\epsilon > 0$ .

## PHASE SEGREGATION IN PdRh ALLOYS

The Pd-Rh alloy system provides a convenient test case for application of the methodology because of its particularly simple phase diagram, which consists of only the liquid and a fcc solid solution phases.

Figure 2(a) shows the EPI profile as a function of distance for  $Pd_{50}Rh_{50}$  alloy. The dominant pair interaction  $V_1$  is negative and the plot illustrates the rapidly convergent properties of the pair interactions as a function of distance. In table 2 we present the comparison between the numerical values of pair interactions up to fourth nearest neighbors for  $Pd_{50}Rh_{50}$  as obtained by the KKR-CPA-GPM<sup>10</sup> and in the present methodology. The agreement of the numerical values between two different methodologies is reasonable and better compared to PdV alloy system. Pd-Rh being a simpler system, in the context of much smaller charge transfer and the amount of disorder present between the constituents, the difference between the two methodologies may not have significant contributions.

We calculate the quantity  $V(k)$  by inverse Fourier transform, by summing  $V_n$  up to the six shell of neighbors. This method favorably contrasts with the evaluation of  $V(k)$  directly in  $k$ -space and is justified by the fast convergence of  $V_n$  with the shell number

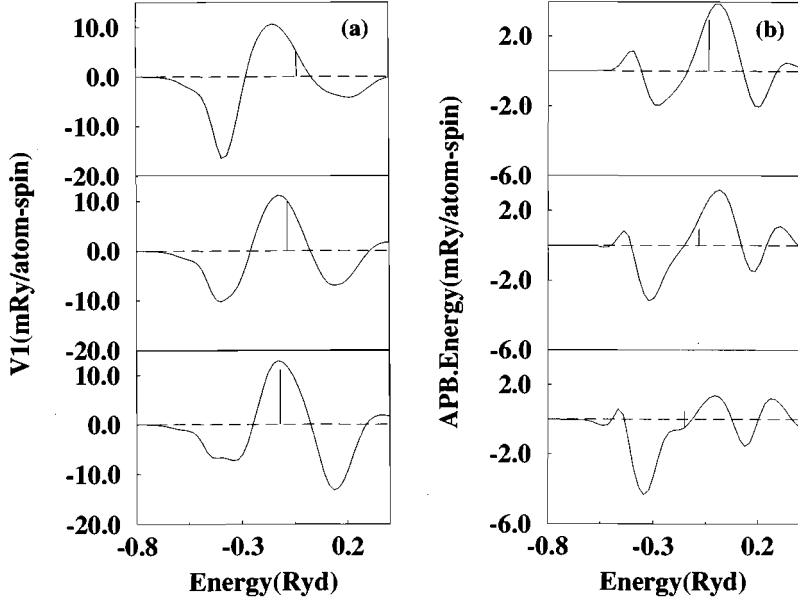


Figure 1: (a) The nearest neighbor pair interactions and (b) antiphase boundary energies as functions of energy for  $\text{Pd}_x\text{V}_{1-x}$  alloys :  $x=0.25$ ,  $x = 0.5$  and  $x = 0.75$  ( from top to bottom). Vertical lines mark the Fermi energy for the three different concentrations.

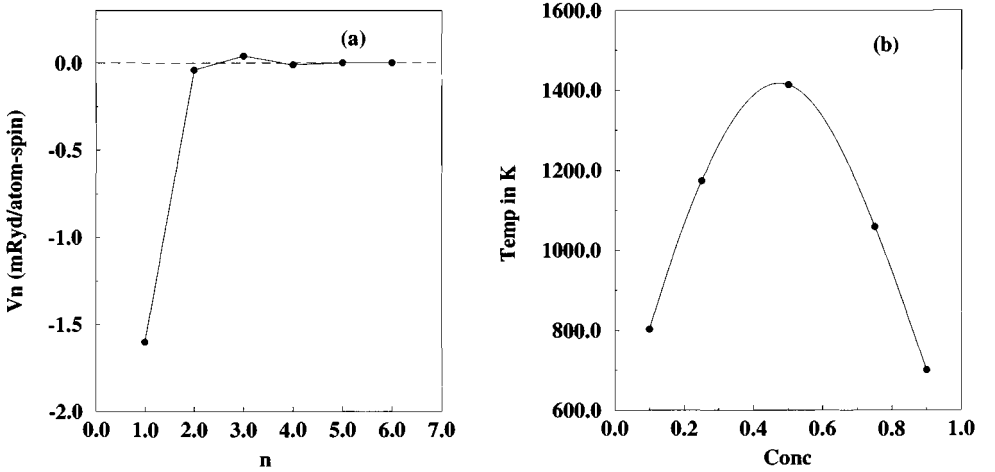


Figure 2: (a) The pair interaction  $V_n$  as a function of distance  $\text{Pd}_{50}\text{Rh}_{50}$  alloy. (b) Spinodal curve for  $\text{Pd}_x\text{Rh}_{1-x}$  alloy system . The points indicate calculated points while the solid line is the cubic spline fit through the points.

as evident from table 2 and figure 2(a). Within the Bragg-Williams approximation the stability limit temperature  $T_o$  at a particular concentration can be related to the minimum of  $V(k)$  profile by

$$T_o = -V(k)x(1-x)/K_B$$

In Figure. 2(b) we plot the stability limit temperatures for Pd-concentration  $x = 0.1, 0.25, 0.5, 0.75$  and  $0.9$ . The points outline a roughly parabolic curve, associated with the spinodal line of decomposition. We note that the temperature at  $x = 0.25$  is larger than that at  $x = 0.75$ . This is in agreement with the experimentally observed asymmetry in the miscibility gap which defines the phase boundary between the solid solution phase and phase separation<sup>14</sup>.

## CONCLUSION

Our results demonstrate that the augmented space recursion and the orbital peeling method in conjunction with the LMTO formalism, constitute a viable and computationally feasible approach to the calculation of phase stability in binary substitutionally disordered alloys.

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# EXPERIMENTAL STUDY OF THE SHORT RANGE ORDER IN THE PT-V SYSTEM: EFFECTIVE PAIR INTERACTIONS AS A FUNCTION OF THE CONCENTRATION

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## INTRODUCTION

We present a detailed study of interactions in two alloys,  $Pt_3V$  and  $Pt_8V$ , and preliminary results on  $Pt_4V$ . *In situ* neutron scattering experiments were performed in order to measure the short range order parameters in the disordered phase for the two concentrations. We will show the drastic effect of the concentration on the Short Range Order (SRO), particularly in  $Pt_8V$ , where the diffuse intensity maxima do not peak at special points of the fcc lattice. Using inverse Monte Carlo (IMC) simulations, two sets of Effective Pair Interactions (EPI) were deduced from the experimental SRO parameters within the Ising Model. Surprisingly, despite quite different SRO patterns, the EPI seem nearly concentration independent. We will show, using MC simulation, that the two very different diffuse intensity maps are well reproduced with the same interaction set. The concentration independence of the EPI allowed us to describe also properties of the ordered states and more generally the whole phase diagram. In particular, we predict the existence, at very low temperature, of a new phase of stoichiometry  $A_5B$  which has never been observed until now.

## LATTICE GAS INTERPRETATION

We define a fcc lattice and affect at each site  $n$ , a spin or an occupation variable  $\sigma_n$  which takes the value  $+1$  or  $-1$  depending on whether site  $n$  is occupied by a A or B atom. Within the generalized perturbation method<sup>1,2</sup>, it has been shown that substitutional binary alloys  $A_cB_{1-c}$  may be described within a Ising model with effective pair interactions with concentration dependence. Thus, the energy of a configuration  $c_i = (\sigma_1, \sigma_2, \dots)$  among the  $2^N$  accessible configurations for one system can be written

as:

$$H = \sum'_{nm} V_{nm} \sigma_n \sigma_m + h \sum_n \sigma_n$$

where the prime indicates that each pair of site (nm) has been counted once.  $h$  is the chemical potential difference and  $V_{nm}$  are the effective pair interactions (EPI) which depend only on the relative vector  $\vec{R}_{nm} = \vec{r}_n - \vec{r}_m$  between sites.

In principle, the  $V_{mn}$  could be deduced from electronic structure calculations, but the smallest ones amount only to fractions of meV, whereas the calculations deal with binding energies, i.e. some eV: it can be understood why the calculation techniques are not yet sufficiently accurate to compute detailed interactions, and why we find it better, until now, to extract them from local order parameters:

$$\alpha(\vec{R}_{nm}) = (\langle \sigma_n \sigma_m \rangle - \langle \sigma_n \rangle \langle \sigma_m \rangle) / 4c(1 - c)$$

Those Warren-Cowley parameters have been determined in situ above the order-disorder transition temperature by diffuse neutron scattering. From these experimentally determined static correlations, the first nine effective pair interactions have been deduced using inverse Monte Carlo simulations.

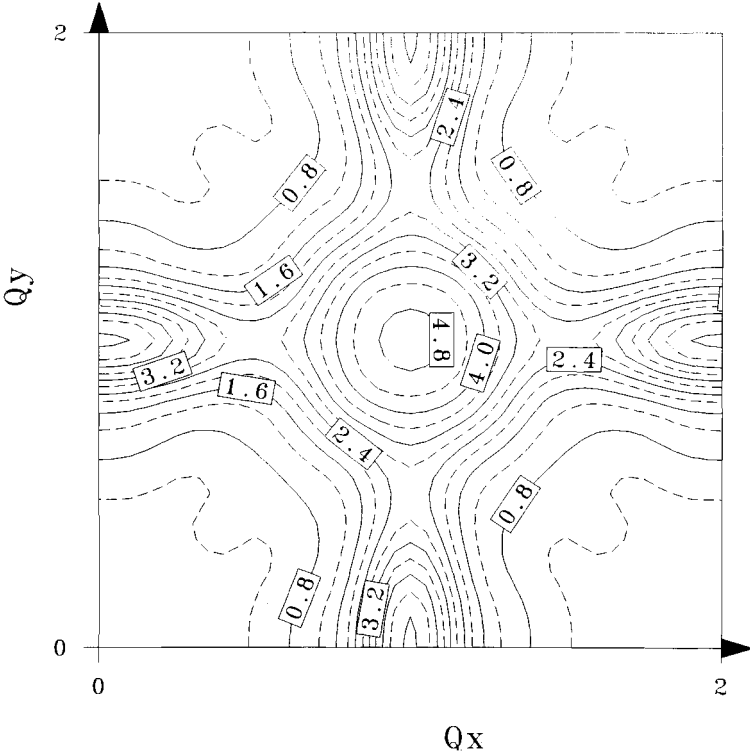


**Figure 1.** Experimental SRO  $\alpha(q)$  in  $Pt_3V$  at  $T=1393$  K in the  $[100]$  plane (Laue units).

## EXPERIMENTAL RESULTS

$Pt_3V$  and  $Pt_8V$  have been investigated at 1393 K and 1224 K respectively and we have explored the [100] and [110] planes of the reciprocal lattice. The measured intensities have been interpreted in a Sparks and Borie approach<sup>3</sup> with first order displacements parameters and using a model including 29  $\alpha(R)$  for  $Pt_3V$  and 21 for  $Pt_8V$ . In figure 1 is displayed the intensity distribution due to SRO  $\alpha(q)$  in the [100] plane. As for  $Pd_3V$ <sup>4</sup>, the diffuse intensity of  $Pt_3V$ <sup>5</sup> is spread along the (100) axes with maxima at the (100) positions, whereas the ground state is built on  $(1 \frac{1}{2} 0)$  concentration wave ( $D0_{22}$  phase).

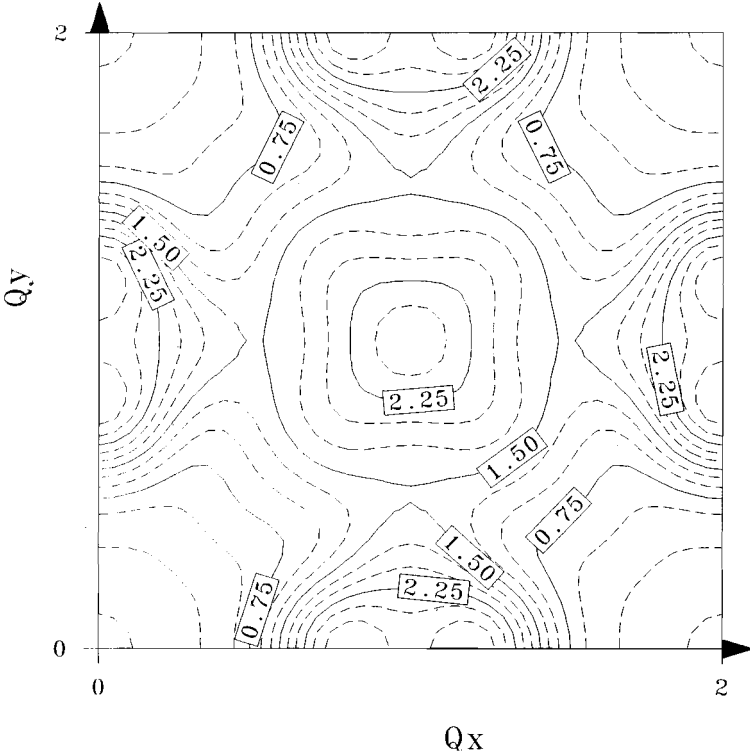


**Figure 2.** Experimental SRO in  $Pt_8V$  at  $T=1224$  K in the [100] plane (Laue units).

Surprisingly, we observe an drastic effect of the concentration on the SRO contribution (figure 2): indeed, in  $Pt_8V$ , the maxima are no longer located at a special point of the fcc lattice but the (100) intensity is splitted perpendicularly in the (010) direction and presents a saddle point at (100) position. Notice that these two maxima are not located just above Bragg peaks of the ordered state: the  $A_8B$  ground state presents Bragg peaks at  $(\frac{2}{3}00)$  and equivalent positions whereas the SRO maxima peak between  $(\frac{2}{3}00)$  and (100).

# DETERMINATION OF THE EFFECTIVE PAIR INTERACTIONS AND DISCUSSION

Using successively an inverse Cluster Variation Method and an IMC algorithm, we determined a set of nine interactions for each alloy (for the IMC procedure, we used a lattice size of  $4 * 24^3$ ). For each alloy, the output from the inverse procedure has been used as an input interaction set in a direct MC simulation, in order to calculate a

| $\langle V(\vec{R}) \rangle$ | $V_1$ | $V_2$ | $V_3$ | $V_4$ | $V_5$ | $V_6$ | $V_7$ | $V_8$ | $V_9$ |
|------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| V(Pt3V)                      | 44.5  | -7    | 6.3   | 5.6   | 4.9   | 0.19  | -0.88 | 2.3   | -4    |
| V(Pt8V)                      | 53.9  | -12.8 | 7.2   | 9.8   | -0.8  | -2.3  | -0.07 | 0.5   | -4.4  |

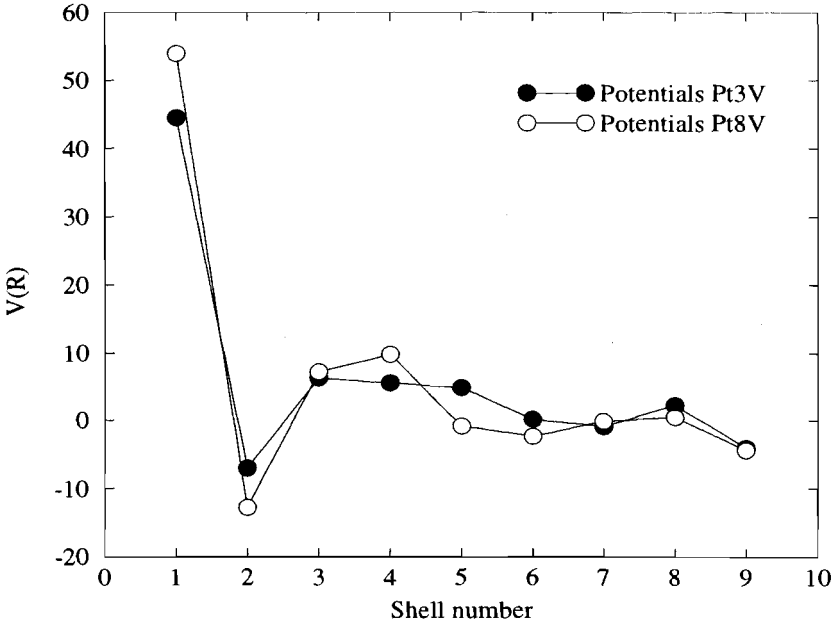


**Figure 3.** Compared effective pair interaction for the two sets  $Pt_3V$  and  $Pt_8V$  in meV.

diffuse intensity map. The agreement with the experimental maps is very good.

Surprisingly, despite very different diffuse intensity maps, we find nearly concentration independent interactions (figure 3). The similarity between the two sets of interactions is unexpected since there is an important difference of concentration between the two samples, and the experiments have been done at different temperatures. Meanwhile, this proves that the long ranged interactions ( $V_5, \dots, V_9$ ) are significant. In particular,  $V_9$  (which corresponds to the vector  $(\frac{3}{2}\frac{3}{2}0)$ , in units of the fcc cube) is relatively high and stable for both sets.

According to electronic structure calculations<sup>1</sup> in parent systems, we observe a increase of  $V_1$  when the platinum concentration increases. Nevertheless this evolution seems to be small.

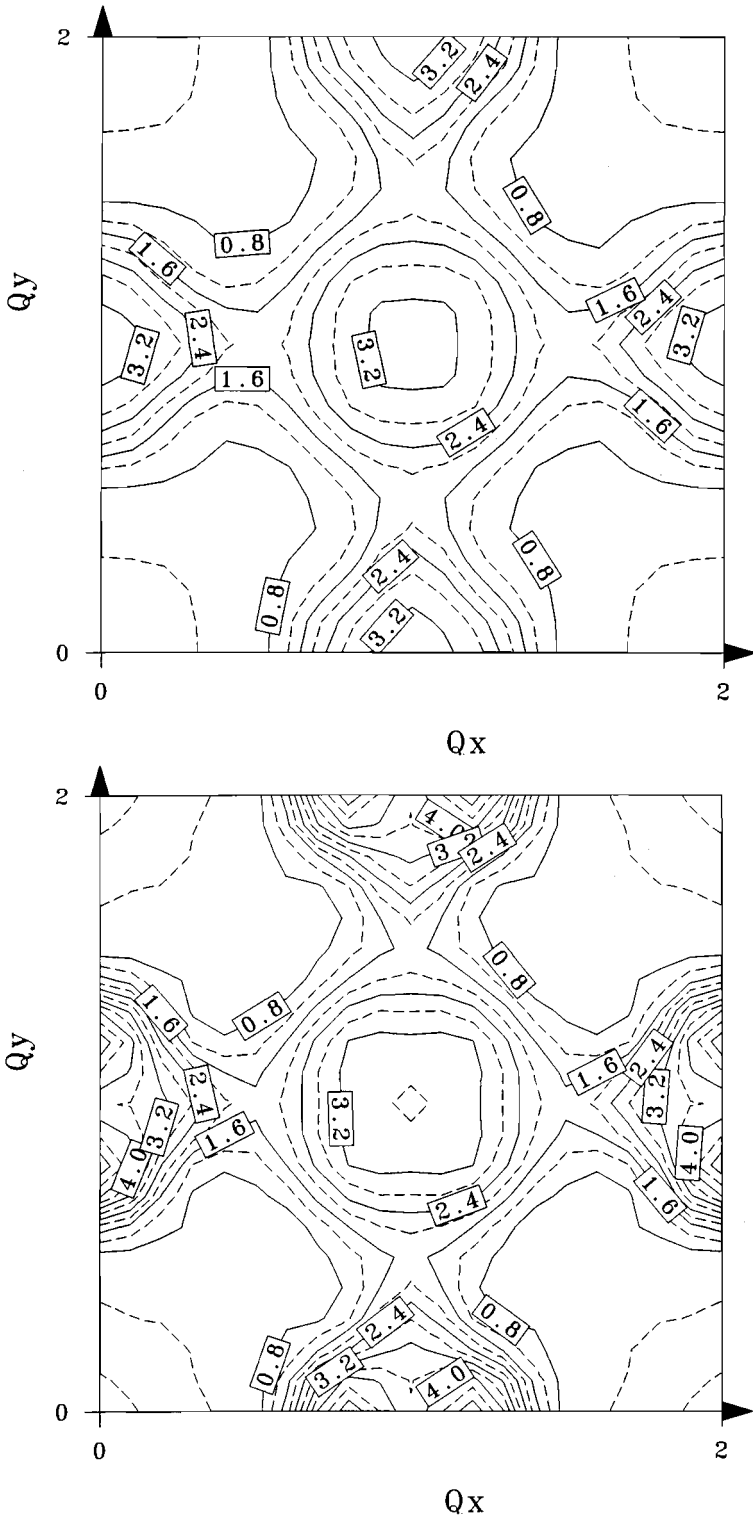


**Figure 4.** Evolution of the simulated SRO (Laue units): at  $c=1/9$  as a function of the temperature with the set found with  $Pt_3V$  in the  $[100]$  plane (a):  $T-T_c=250$  K and (b):  $T-T_c=50$  K.

Furthermore, a hierarchy of the potentials is expected, due to the geometry of the fcc lattice. As the second, first and fourth can be reached by two first neighbours steps only and the further neighbours require more steps, we observe, especially with the  $Pt_8V$  set, the corresponding hierarchy<sup>1</sup>:  $|V_1| \gg |V_2, V_3, V_4| \gg |V_5, V_6, \dots|$ . The fact that we observe this fcc hierarchy between the  $V$ 's and their concentration independence gives us confidence in the model and our procedure.

We now use the interaction sets found for both compositions to find the ground state and to calculate transition temperatures.

For  $Pt_3V$ , we find that the ground state is highly degenerated between the structures  $L1_2$ ,  $DO_{22}$  and  $DO_{23}$ . Indeed, the energy differences between these phases are smaller than 2 meV. This is in complete agreement with the experimentally observed degeneracy<sup>6,7</sup> in  $Pt_3V$ : a small change of the electronic concentration (by adding a few per cent of rhodium) leads to a sequence of long period structures that interpolate between  $L1_2$  and  $DO_{22}$ <sup>8</sup>. As for the transition temperature between the ordered state and the disordered phase, we find, using a Monte-Carlo simulation,  $T_c^{cal} = 1100$  K, whereas the experimental value is  $T_c^{exp} = 1288$  K.

For  $Pt_8V$ , we find that the ground state is the experimentally observed  $A_8B$  phase<sup>6,9</sup>. The fact that we find the correct ground state is a strong indication of the relevance of the long range part of our interaction set. Indeed, with only four interactions, the ground state at composition  $c = \frac{1}{9}$  is degenerated between many  $A_8B$  structures<sup>10</sup>. Of course, this degeneracy is expected to be lifted by the interactions that extend beyond  $V_4$ . It happens that the numerical values we found for these interactions are such that the degeneracy is lifted in favour of the experimentally observed  $A_8B$  phase. Finally, the calculated transition temperature is  $T_c^{cal} = 850$  K, which is to be compared to the experimental value  $T_c^{exp} = 1090$  K.

As explained above, despite the fact that the interactions do not depend on the concentration, the diffuse intensity maps of  $Pt_3V$  and  $Pt_8V$  are very different. This behavior is in total contradiction with a mean field approach: According to the Krivoglaz-Clapp-Moss formula<sup>11</sup>, a minimum of  $V(\vec{q})$  corresponds of a maximum of  $\alpha(\vec{q})$ . So, if the  $V$ 's do not change with the concentration, the mean field approach cannot explain the topology changes observed in the diffuse intensity maps.

The above result show that the concentration dependance of the intensity maps is purely a statistical mechanics effect. In order to illustrate this important conclusion, we calculate  $\alpha(\vec{q})$ , in the disordered state, at concentration  $c = \frac{1}{9}$ , with the  $V$ 's obtained at the composition  $Pt_3V$  (figure 4). 150 K above the transition temperature, we indeed observe the experimentally observed splitting of the diffuse intensity maxima, with a saddle point at (100).

## CONCLUSION

We have measured the experimental SRO contribution in  $Pt_3V$  and  $Pt_8V$  alloys. The  $Pt_3V$  SRO displays maxima at (100) positions despite a ground state built with the  $(1\frac{1}{2}0)$  concentration wave. For  $Pt_8V$ , the maxima are not located at special points of the fcc lattice.

The most important result of this work is that despite two different SRO patterns, we have found concentration independent EPI. The evolution of the diffuse intensity with composition is thus mainly due to the sensitivity of the equilibrium state (i.e. the correlation function) to the concentration.

Our results gives us a very good confidence in those potentials and more generally in our EPI determination method: with these two sets of potentials we found for two sam-

ples, at two different temperatures, we were able to (i) reproduce fine degeneracy effects between long period structures at  $A_3B$  stoichiometry, (ii) stabilize the experimentally observed  $A_8B$  structure, (iii) reproduce the two different diffuse intensity maps at  $c = \frac{1}{4}$  and  $c = \frac{1}{9}$ . Furthermore, we predict the stability, at very low temperature, of a phase of composition  $A_5B$ , which has never been observed until now.

## Acknowledgements

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## ANALYSIS OF THE EFFECTIVE INTERATOMIC INTERACTIONS IN METALLIC ALLOYS

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### INTRODUCTION

Ab-initio studies of alloy phase stability are usually based on the Ising-type Hamiltonian, whose parameters, often called the effective cluster interactions (ECI), serve as an input in determination of the equilibrium properties of the system via the methods of statistical mechanics. An alternative formulation, which completely avoids determination of ECIs by calculating the electronic structure and solving the statistical part of the problem in one step, is employed in the concentration-wave method<sup>1</sup>. It is based on the grandcanonical potential  $\Omega$  configurationally averaged<sup>2</sup> within the coherent potential approximation (CPA) and on a mean-field solution of the statistical part of the problem including usually also the Onsager cavity field.

The ECIs can be determined either by the Connolly-Williams inversion scheme (CWIS)<sup>3</sup> which extracts the ECIs from total energies of suitably chosen periodic or disordered structures, or by the generalized perturbation method (GPM)<sup>4</sup>. The GPM is based on the force theorem<sup>5</sup> according to which only the band energy term of the total energy of a completely disordered alloy described within the CPA is expanded in occupation indices. Within the GPM, in contrast to the Connolly-Williams scheme, the double-counting and electrostatic terms are neglected. An attempt to overcome this limitation in the bulk case appeared<sup>6</sup> recently. The Ising-type Hamiltonians obtained from the CWIS and from the GPM are not identical from several reasons. The Connolly-Williams method yields concentration independent ECIs, and it corresponds to the grandcanonical ensemble, while the GPM corresponds to a canonical ensemble for a fixed value of the alloy concentration. The ECIs determined by the GPM thus depend on the alloy concentration. The mutual relation between these two approaches is not straightforward<sup>7-11</sup>.



It turns out that for some systems the GPM yields the pair interactions, particularly those between first neighbors, which do not correspond to experimental phase diagrams. It is the purpose of the present work to show some of these cases and make a comparison with results obtained by other methods, particularly by the CWIS.

## METHODOLOGY

Let us consider a binary system  $A - B$ . Its particular configuration is determined by a set of occupation indices  $\eta_i$ , where  $\eta_i = 1$  if the site  $i$  is occupied by an atom of the type  $A$ , and  $\eta_i = 0$  otherwise. This form corresponds to the lattice gas model. The effective concentration-independent Ising Hamiltonian reads

$$H = NE_0 + \sum_i D_i \eta_i + \frac{1}{2} \sum_{ij} V_{ij} \eta_i \eta_j + \frac{1}{3} \sum_{ijk} T_{ijk} \eta_i \eta_j \eta_k + \frac{1}{4} \sum_{ijkl} Q_{ijkl} \eta_i \eta_j \eta_k \eta_l + \dots \quad (1)$$

Here,  $E_0$  is the total energy per atom of the pure system  $B$ , and  $V$ ,  $T$ ,  $Q$ , etc., denote the interactions of a pair, triplet, quadruplet, etc. of atoms, respectively. The other form, explicitly dependent on the concentration  $c$  can be written as

$$\begin{aligned} h(c) = Ne(c) &+ \sum_i d_i(c) \delta\eta_i + \frac{1}{2} \sum_{ij} v_{ij}(c) \delta\eta_i \delta\eta_j + \frac{1}{3} \sum_{ijk} t_{ijk}(c) \delta\eta_i \delta\eta_j \delta\eta_k \\ &+ \frac{1}{4} \sum_{ijkl} q_{ijkl}(c) \delta\eta_i \delta\eta_j \delta\eta_k \delta\eta_l + \dots \end{aligned} \quad (2)$$

where  $\delta\eta_i = \eta_i - c$ . The interatomic interactions in (1) and (2) are, by definition, equal to zero, if, at least two site indices coincide. The Ising Hamiltonian (1) is usually determined by the Connolly-Williams method, while the parameters of (2) are usually calculated using the GPM.

Due to the linear independence of occupation indices  $\eta_i$  the concentration-dependent parameters can be determined from the concentration-independent ones. In the special case of interactions limited to the fourth order and nearest neighbors one finds for fcc-based alloys

$$\begin{aligned} e(c) &= E_0 + Dc + 6Vc^2 + 16Tc^3 + 12Qc^4, \quad d(c) = D + 12Vc + 48Tc^2 + 48Qc^3, \\ v(c) &= V + 8Tc + 12Qc^2, \quad t(c) = T + 3Qc, \quad q(c) = Q. \end{aligned} \quad (3)$$

The quantity  $v(c)$  and the disordered-alloy formation energy (mixing energy)

$$\begin{aligned} E_d(c) &= E(A_c B_{1-c}) - c E(A) - (1-c) E(B) = \\ &= -c(1-c)[6V + 8T(1+c) + 12Q(1+c+c^2)] \end{aligned} \quad (4)$$

are used in further analysis.

First, we have used the original formulation<sup>3</sup> of the CW method to determine five interaction parameters  $E_0, D, V, T$ , and  $Q$  up to quadruplets for the nearest neighbors in the fcc lattice. The total energies were calculated for five ordered alloys, namely, two pure elements  $A$  and  $B$ ,  $AB$  compound in the  $L1_0$  structure and the  $A_3B$  and  $AB_3$  compounds in the  $L1_2$  structure. The *ab initio* electronic-structure calculations were performed using the local density approximation and the full-potential linearized augmented plane wave (FP-LAPW) method as implemented in the package WIEN95<sup>12</sup>. All calculations were nonrelativistic. The exchange-correlation potential of Perdew and

Wang<sup>13</sup> was used. The total energies were converged to 0.1 mRy/atom. The number of  $k$  points was chosen so as to correspond to 120 points in the irreducible wedge of the Brillouin zone of the fcc structure, the energy cut-off was 16 Ry. We have tested various values of these parameters and it turned out that the present choice is sufficient to achieve desired uniform accuracy for all structures. For each structure the total energy was minimized with respect to the lattice constant. These interaction parameters correspond to the locally relaxed parameters<sup>14</sup> and are denoted by superscript *CW*.

Second, using the fully relativistic version of the TB-LMTO-CPA method<sup>15</sup> within the atomic sphere approximation (ASA) we have calculated the total energies for random alloys  $A_xB_{1-x}$  at five concentrations,  $x = 0, 0.25, 0.5, 0.75$  and 1, and using the CW method modified for disordered alloys<sup>16</sup> we have determined five interaction parameters  $E_0, D, V, T$ , and  $Q$  as before (superscript *RA*). Finally, the electronic structure of random alloys calculated by the TB-LMTO-CPA method served as an input of the GPM<sup>17,18</sup> from which the pair interactions  $v(c)$  (superscript *GPM*) were determined. In order to eliminate the charge transfer effects in these calculations, the atomic radii were adjusted in such a way that atoms were charge neutral while preserving the total volume of the alloy.<sup>19,20</sup> The quantity  $v^{GPM}(c)$  used for comparisons is a sum of properly weighted interactions  $v_{ij}^{GPM}(c)$ .

We have employed the Bragg-Williams approximation (BWA) to obtain rough estimates of the ordering/segregation critical temperatures. It is well known that the BWA usually overestimates critical temperatures (approximately by 20 %) in comparison with the 'exact' value obtained from Monte Carlo simulations, or by other highly accurate methods of statistical mechanics. This order of accuracy is nevertheless sufficient for our present purposes.

## RESULTS AND DISCUSSION

In order to check the consistency and mutual relations of ECIs calculated by various methods, as well as to compare them with experimental data, we have performed calculations for several alloy systems, as diverse as Cu-Ni, Al-Li, Al-Ni, Ni-Pt and Pt-Rh. Here we present the results for Al-Ni, Pt-Rh and Ni-Pt alloys in some detail, because the pair interactions between the first neighbors are dominant in these alloys which makes the interpretation relatively simple. On the other hand, the pair interactions between more distant neighbors and also triplet interactions are important for Al-Li and Cu-Ni. The equilibrium atomic radii, bulk moduli and electronegativities of Al and Ni are rather different, while Pt and Rh are quite similar in this respect. The Ni and Pt atoms differ mainly by their size.

The mixing energies for Al-Ni system  $E_d^{CW}(c)$  and  $E_d^{RA}(c)$  are almost identical, reaching their minimal values approx.  $-28.9$  mRy and  $-29.3$  mRy at 43 at. % and 40 at. % Al, respectively. The pair interactions  $v^{CW}(c)$ ,  $v^{RA}(c)$  and  $v^{GPM}(c)$  are shown in Fig. 1. The mixing energies agree rather well with the results of Pasturel et al.<sup>21</sup> and those of Abrikosov et al.<sup>16</sup>. The pair interaction  $v^{CW}(c)$  is in a very good agreement with the locally relaxed quantity given by Carlsson<sup>14</sup>, and also it is rather similar to the effective pair interaction found by Pasturel et al.<sup>21</sup>, although it is smaller approximately by a factor 0.7. The pair interaction  $v^{RA}(c)$  differs from the corresponding quantity reported by Abrikosov et al.<sup>16</sup>, which can be probably attributed to different computational schemes, as we assume neutral spheres, while Abrikosov et al. suppose equal sphere radii. The pair interaction  $v^{GPM}(c)$  closely follows  $v^{CW}(c)$  for Ni-rich alloys and  $v^{RA}(c)$  for Al-rich alloys, at intermediate concentrations all three quantities

are almost identical. Theoretical results, i.e., large negative mixing energies and large positive pair interactions agree well with the experimental phase diagram<sup>22</sup> which consists of two solid solutions (Al) and (Ni), and of several ordered intermetallic phases that are stable up to the melting point.

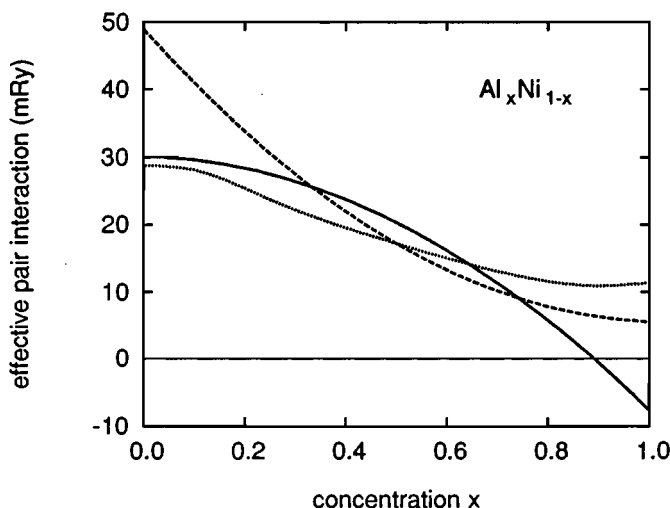


**Figure 1.** The effective pair interactions as functions of alloy composition for the alloy system Al-Ni. The results of the CWIS based on the FP-LAPW calculations for 5 ordered structures (full line) and on the TB-LMTO-CPA for 5 disordered alloys (dash line) are compared with the results of the GPM (dotted line).

The mixing energies for Pt-Rh system  $E_d^{CW}(c)$  and  $E_d^{RA}(c)$  are positive and similar,  $E_d^{CW}(c)$  has maximum (approx. 1.7 mRy) at 54 at. % Pt, while the maximum of  $E_d^{RA}(c)$  (approx. 1.5 mRy) lies at 38 at. % Pt. This picture agrees with the experimental phase diagram<sup>22</sup> which displays a continuous set of solid solutions over the whole range of concentrations for temperatures above 1033 K; at lower temperatures there is a miscibility gap. The pair interactions are shown in Fig. 2. The interactions  $v^{CW}(c)$  and  $v^{RA}(c)$  are both negative, which is in a qualitative agreement with the experimental phase diagram. On the other hand, the pair interaction  $v^{GPM}(c)$  calculated within the GPM is positive in the whole concentration range, which contradicts not only the experimental data, but also the Connolly-Williams results obtained from FP-LAPW calculations for ordered structures as well as those found from the TB-LMTO-CPA calculations for disordered alloys.

The mixing energies for Ni-Pt system  $E_d^{CW}(c)$  and  $E_d^{RA}(c)$  are negative,  $E_d^{CW}(c)$  has minimum ( $-2.0$  mRy) at 55 at. % Ni, while the minimum of  $E_d^{RA}(c)$  ( $-10.2$  mRy) lies at 62 at. % Ni. There is only very rough qualitative agreement with the experimental phase diagram<sup>22</sup> which shows a complete solid solubility at high temperatures, and two ordered phases NiPt and Ni<sub>3</sub>Pt with critical temperatures 918 and 853 K, respectively. The pair interaction  $v^{CW}(c)$  is a small positive quantity not exceeding 3 mRy, and  $v^{RA}(c)$  is strongly increasing from 2 mRy for Pt-rich alloys to 23 mRy for Ni-rich alloys. The pair interaction  $v^{GPM}(c)$  is again increasing from Pt to Ni and attains even higher values (between 13 and 28 mRy). At the composition Ni<sub>0.5</sub>Pt<sub>0.5</sub>,  $v^{GPM}(0.5) = 18$  mRy, which compares quite favorably with 16 mRy calculated by Singh et al.<sup>20</sup>, but it

is in disagreement with the low critical temperature of the ordered phase NiPt.

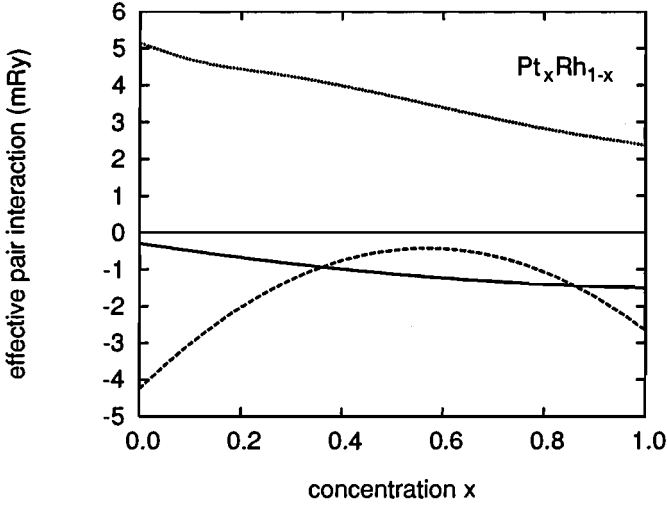


Figure 2. The same as figure 1, but for Pt-Rh.

## CONCLUSIONS

We have found that for some alloys (e.g. Pt-Rh and Ni-Pt), the GPM yields pair interactions which are incorrect, because their values are either too large and would lead to overestimated transition temperatures (Ni-Pt), or they have even opposite sign than that expected from the experimental phase diagram and predicted by other theoretical methods (Pt-Rh). Various explanations of these discrepancies are conceivable:

- (i) The neglect of the local environment effects, i.e., the vertex corrections connected with the concentration fluctuations. These corrections are approximately included in the concentration-wave method<sup>1</sup>, and represent the linear response of a system to the concentration fluctuations.
- (ii) Neglect of lattice relaxations due to the different sizes of atoms and of the corresponding elastic energy connected with local deformations of the lattice.
- (iii) Possible violation of the force theorem. This would mean that the contributions from double counting terms should be considered.

We conclude that more work is needed. In particular it would be useful to repeat the TB-LMTO-CPA calculations using also other methods for description of charge transfer effects, e.g., the so-called correlated CPA<sup>23</sup>, or the screened-impurity model<sup>24</sup>. One may also ask if a full treatment of relativistic effects is necessary. The answer is positive<sup>20</sup>, at least for some alloys (Ni-Pt) that contain heavy elements.

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# APPLICATION OF CONTINUOUS DISPLACEMENT TREATMENT OF CVM TO BINARY ALLOY SYSTEMS

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## 1. Introduction

Statistical mechanics methods such as Cluster Variation Method (CVM) designed for working with lattice statics are based on the assumption that atoms sit on lattice points. We extend the conventional CVM [1] and present a method of taking into account continuous displacement of atoms from their reference lattice points. The basic idea is to treat an atom which is displaced by  $\mathbf{r}$  from its reference lattice point as a species designated by  $\mathbf{r}$ . Then the summation over the species in the conventional CVM changes into an integral over  $\mathbf{r}$ . An example of the 1-D case was done successfully before [2]. The similar treatments have also been done for pure 2-D systems [3,4] as well as for lattice defects in 2-D crystals [5]. It is the purpose of the present paper to investigate the local lattice distortion on the alloy phase stability by using the continuous CVM.

We work with the pair approximation of a binary alloy system. The two species are written as A and B ( $i=1$  and  $2$ ), and we do not include vacancies. The nearest-neighbour (NN) interactions are taken into account, and the numerical examples are given for a 2-D square lattice as well as for an fcc lattice. Although we consider thermal vibrations, we assume the temperature is high enough so that the classical treatment is applicable and the equipartition law of the kinetic energy is justified. Therefore, we work only on the potential energy part of the partition function.

## 2. Principle of the Continuous CVM

The atomic displacements from reference sites  $i$  and  $j$  are written as  $\mathbf{r}_i$  and  $\mathbf{r}'_j$ . The vector from the  $i$  atom at P to the  $j$  atom at Q is  $\mathbf{a} + \mathbf{r}'_j - \mathbf{r}_i$ , where  $\mathbf{a}$  denotes the lattice spacing vector. For the pair variables, we distinguish three kinds of pair distribution functions  $g_{ij}$ , and use three potentials  $\epsilon_{ij}$ :

$$\epsilon_{ij}(\mathbf{r}_i, \mathbf{r}'_j) = \epsilon_{ij}(|\mathbf{a} + \mathbf{r}'_j - \mathbf{r}_i|) \quad (1)$$

Firstly, we consider 2-D square lattice with nearest-neighbour interactions.

The symmetry constraint for the 2D square lattice is written as:

$$f_i(\mathbf{r}_i) = \sum_{j=1}^2 \int g_{ij}(\mathbf{r}_i, \mathbf{r}'_j) d\mathbf{r}'_j = \sum_{j=1}^2 \int g_{ij}(\mathbf{R}^{-1}\mathbf{r}_i, \mathbf{r}'_j) d\mathbf{r}'_j, \quad (2)$$

where  $f_i(\mathbf{r}_i)$  represents the point probability function at the site  $i$  and  $\mathbf{R}$  denotes a symmetry operator of  $90^\circ$  rotation, which brings a vector  $\mathbf{r}$  into  $\mathbf{R}\mathbf{r}$ . Multiplying this with a Lagrange multiplier  $\alpha_i(\mathbf{r}_i)$ , we obtain

$$\begin{aligned} C_\alpha &= 4 \sum_{i=1}^2 \int d\mathbf{r}_i \alpha_i(\mathbf{r}_i) \sum_{j=1}^2 \left( \int g_{ij}(\mathbf{r}_i, \mathbf{r}'_j) d\mathbf{r}'_j - \int g_{ij}(\mathbf{R}^{-1}\mathbf{r}_i, \mathbf{r}'_j) d\mathbf{r}'_j \right) \\ &= 4 \sum_{i=1}^2 \sum_{j=1}^2 \left( \int d\mathbf{r}_i \alpha_i(\mathbf{r}_i) \int g_{ij}(\mathbf{r}_i, \mathbf{r}'_j) d\mathbf{r}'_j - \int d\mathbf{r}_i \alpha_i(\mathbf{R}\mathbf{r}_i) \int g_{ij}(\mathbf{r}_i, \mathbf{r}'_j) d\mathbf{r}'_j \right) \\ &= 4 \sum_{i=1}^2 \sum_{j=1}^2 \int d\mathbf{r}_i \int d\mathbf{r}'_j (\alpha_i(\mathbf{r}_i) - \alpha_i(\mathbf{R}\mathbf{r}_i)) g_{ij}(\mathbf{r}_i, \mathbf{r}'_j). \end{aligned} \quad (3)$$

For 2D square lattice, a  $180^\circ$  rotation symmetry leads to

$$g_{ij}(\mathbf{r}_i, \mathbf{r}'_j) = g_{ji}(-\mathbf{r}'_j, -\mathbf{r}_i). \quad (4)$$

Using this, we can write eq.(2) as

$$C_\alpha = 4 \sum_{i=1}^2 \sum_{j=1}^2 \int d\mathbf{r}_i \int d\mathbf{r}'_j ((\alpha_j(-\mathbf{r}'_j) - \alpha_j(-\mathbf{R}\mathbf{r}'_j))) g_{ij}(\mathbf{r}_i, \mathbf{r}'_j) \quad (5)$$

Adding (2) and (4), and dividing the sum by 2, we obtain

$$\begin{aligned} C_\alpha &= 2 \sum_{i=1}^2 \sum_{j=1}^2 \int d\mathbf{r}_i \int d\mathbf{r}'_j (\alpha_i(\mathbf{r}_i) - \alpha_i(\mathbf{R}\mathbf{r}_i)) g_{ij}(\mathbf{r}_i, \mathbf{r}'_j) \\ &\quad + 2 \sum_{i=1}^2 \sum_{j=1}^2 \int d\mathbf{r}_i \int d\mathbf{r}'_j ((\alpha_j(-\mathbf{r}'_j) - \alpha_j(-\mathbf{R}\mathbf{r}'_j))) g_{ij}(\mathbf{r}_i, \mathbf{r}'_j) \end{aligned} \quad (6)$$

We may then define

$$\gamma_i(\mathbf{r}_i) = \alpha_i(\mathbf{r}_i) - \alpha_i(\mathbf{R}\mathbf{r}_i) \quad (7)$$

to write the above eq.(5) as

$$C_\alpha = 2 \sum_{i=1}^2 \sum_{j=1}^2 \int d\mathbf{r}_i \int d\mathbf{r}'_j (\gamma_i(\mathbf{r}_i) + \gamma_j(-\mathbf{r}'_j)) g_{ij}(\mathbf{r}_i, \mathbf{r}'_j) \quad (8)$$

which corresponds to eq.(3.3) of Ref. 4. It is noted that this expression does not depend on the coordination number.

### 3. Grand potential and its minimum

In order to control the composition of the binary alloy we use the chemical potential  $\mu_i$ , and minimize the grand potential  $\Omega$ . The densities of A and B atoms are obtained from the point distribution function  $f_1(\mathbf{r})$  and  $f_2(\mathbf{r})$  as

$$\rho_1 = \int d\mathbf{r} f_1(\mathbf{r}) \quad ; \quad \rho_2 = \int d\mathbf{r} f_2(\mathbf{r}). \quad (9)$$

As usually done in the CVM treatment, we transform the chemical potential terms in the grand potential (given below)  $\Omega$  as

$$-(\mu_1\rho_1+\mu_2\rho_2)=-\frac{1}{2}((\mu_1+\mu_2)(\rho_1+\rho_2)+(\mu_1-\mu_2)(\rho_1-\rho_2)). \quad (10)$$

We can regard these terms as the Lagrange terms for the constraint on  $\rho_i$ 's. In this case, since  $\rho_1+\rho_2=1$ , we do not need the first constraint term on  $\rho_1+\rho_2$ . Therefore, it means that one can choose

$$\mu_1+\mu_2=0. \quad (11)$$

Taking advantage of the above (11), we may define  $\mu$  as

$$\mu_1=-\mu \quad ; \quad \mu_2=\mu. \quad (12)$$

Then it is straightforward to show that the density of B atoms increases as the parameter  $\mu$  increases.

When we want to calculate for different composition, we do not fix  $\rho_i$  in minimizing the free energy. We rather fix the chemical potential  $\mu$ . The reason is that when we use the chemical potential, we can prove the convergence of the natural iteration method. If we fix the composition instead, natural iteration method (NIM, mentioned below) does not necessarily converge.

For a system of N lattice points, the grand potential is given by

$$\begin{aligned} \Psi = \frac{\beta\Omega}{N} = & 2\beta \sum_{i=1}^2 \sum_{j=1}^2 \int d\mathbf{r}_i \int d\mathbf{r}'_j \varepsilon_{ij}(\mathbf{r}_i, \mathbf{r}'_j) g_{ij}(\mathbf{r}_i, \mathbf{r}'_j) \\ & - \frac{3}{2} \left( \sum_{i=1}^2 \int d\mathbf{r}_i L[f_i(\mathbf{r}_i)] + \sum_{j=1}^2 \int d\mathbf{r}'_j L[f_j(\mathbf{r}'_j)] \right) \\ & + 2 \sum_{i=1}^2 \sum_{j=1}^2 \int d\mathbf{r}_i \int d\mathbf{r}'_j L[g_{ij}(\mathbf{r}_i, \mathbf{r}'_j)] - 1 + \beta\lambda \left( 1 - \sum_{i=1}^2 \sum_{j=1}^2 g_{ij}(\mathbf{r}_i, \mathbf{r}'_j) \right) \\ & + 2 \sum_{i=1}^2 \sum_{j=1}^2 \int d\mathbf{r}_i \int d\mathbf{r}'_j (\gamma_i(\mathbf{r}_i) + \gamma_j(-\mathbf{r}'_j)) g_{ij}(\mathbf{r}_i, \mathbf{r}'_j) \\ & - \frac{\beta}{2} \left( \sum_{i=1}^2 \mu_i \int d\mathbf{r}_i f_i(\mathbf{r}_i) + \sum_{j=1}^2 \mu_j \int d\mathbf{r}'_j f_j(\mathbf{r}'_j) \right). \end{aligned} \quad (13)$$

When we differentiate  $\Psi$  in eq.(13) with respect to  $g_{ij}(\mathbf{r}_i, \mathbf{r}'_j)$ , we derive

$$\begin{aligned} \frac{\partial \Psi}{\partial g_{ij}(\mathbf{r}_i, \mathbf{r}'_j)} = & 2\beta \varepsilon_{ij}(\mathbf{r}_i, \mathbf{r}'_j) - \frac{3}{2} \ln(f_i(\mathbf{r}_i) f_j(\mathbf{r}'_j)) + 2 \ln g_{ij}(\mathbf{r}_i, \mathbf{r}'_j) - \beta \lambda \\ & + 2(\gamma_i(\mathbf{r}_i) + \gamma_j(-\mathbf{r}'_j)) - \frac{\beta}{2} (\mu_i + \mu_j) = 0, \end{aligned} \quad (14)$$

which leads to the basic equation of the present formulation:

$$\begin{aligned} g_{ij}(\mathbf{r}_i, \mathbf{r}'_j) = & \exp\left(\frac{\beta\lambda}{2}\right) \exp(-\beta \varepsilon_{ij}(\mathbf{r}_i, \mathbf{r}'_j) + \frac{\beta}{4} (\mu_i + \mu_j)) (f_i(\mathbf{r}_i) f_j(\mathbf{r}'_j))^{3/4} \\ & \times \exp(-\gamma_i(\mathbf{r}_i) - \gamma_j(-\mathbf{r}'_j)). \end{aligned} \quad (15)$$



#### 4. Minor iteration

In order to get the pair distribution functions  $g_{ij}$ , which satisfy the symmetry constraints, so-called minor iterations must be converged. When we use  $g_{ij}(\mathbf{r}_i, \mathbf{r}'_j)$  of (11) in (2), we obtain the minor equations regarding the rotation operator  $\mathbf{R}$  of the angle  $\pi/2$ :

$$\begin{aligned} & \sum_{j=1}^2 \int d\mathbf{r}'_j \exp(-\beta \varepsilon_{ij}(\mathbf{r}_i, \mathbf{r}'_j) + \frac{\beta}{4} (\mu_i + \mu_j)) (f_i(\mathbf{r}_i) f_j(\mathbf{r}'_j))^{3/4} \\ & \quad \times \exp(-\gamma_i(\mathbf{r}_i) - \gamma_j(-\mathbf{r}'_j)) \\ & = \sum_{j=1}^2 \int d\mathbf{r}'_j \exp(-\beta \varepsilon_{ij}(\mathbf{R}^{-1}\mathbf{r}_i, \mathbf{r}'_j) + \frac{\beta}{4} (\mu_i + \mu_j)) (f_i(\mathbf{R}^{-1}\mathbf{r}_i) f_j(\mathbf{r}'_j))^{3/4} \\ & \quad \times \exp(-\gamma_i(\mathbf{R}^{-1}\mathbf{r}_i) - \gamma_j(-\mathbf{r}'_j)), \end{aligned} \quad (16)$$

where the normalization factor  $\exp(\beta\lambda/2)$  has been canceled. We can bring  $\gamma_i$ 's out of the integrals to write this as

$$\begin{aligned} & \exp(-\gamma_i(\mathbf{r}_i)) \sum_{j=1}^2 \int d\mathbf{r}'_j g_{ij0}(\mathbf{r}_i, \mathbf{r}'_j) \exp(+\gamma_i(\mathbf{r}_i)) \\ & = \exp(-\gamma_i(\mathbf{R}^{-1}\mathbf{r}_i)) \sum_{j=1}^2 \int d\mathbf{r}'_j g_{ij0}(\mathbf{R}^{-1}\mathbf{r}_i, \mathbf{r}'_j) \exp(+\gamma_i(\mathbf{R}^{-1}\mathbf{r}_i)). \end{aligned} \quad (17)$$

The subscript 0 indicates that the normalization factor is not included. We treat  $\gamma$ 's inside the integrals as  $\gamma^{[in]}$  and those outside as  $\gamma^{[out]}$ , and define

$$\Delta\gamma_i(\mathbf{r}_i) = \gamma_i(\mathbf{r}_i)^{[out]} - \gamma_i(\mathbf{r}_i)^{[in]} \quad (18)$$

Then the eq.(17) is rewritten as

$$\exp(-\Delta\gamma_i(\mathbf{r}_i)) \sum_{j=1}^2 \int d\mathbf{r}'_j g_{ij0}^{[in]}(\mathbf{r}_i, \mathbf{r}'_j) = \exp(-\Delta\gamma_i(\mathbf{R}^{-1}\mathbf{r}_i)) \sum_{j=1}^2 \int d\mathbf{r}'_j g_{ij0}^{[in]}(\mathbf{R}^{-1}\mathbf{r}_i, \mathbf{r}'_j) \quad (19)$$

which is

$$\Delta\gamma_i(\mathbf{r}_i) - \Delta\gamma_i(\mathbf{R}^{-1}\mathbf{r}_i) = \ln \left( \frac{\sum_{j=1}^2 \int d\mathbf{r}'_j g_{ij0}^{[in]}(\mathbf{r}_i, \mathbf{r}'_j)}{\sum_{j=1}^2 \int d\mathbf{r}'_j g_{ij0}^{[in]}(\mathbf{R}^{-1}\mathbf{r}_i, \mathbf{r}'_j)} \right) \equiv H_i(\mathbf{r}_i). \quad (20)$$

This corresponds to eq.(5.3) of Ref.4. Or, we may define

$$f_{i0}^{[in]}(\mathbf{r}_i) \equiv \sum_{j=1}^2 \int d\mathbf{r}'_j g_{ij0}^{[in]}(\mathbf{r}_i, \mathbf{r}'_j) \quad (21)$$

to write (20) as

$$\Delta\gamma_i(\mathbf{r}_i) - \Delta\gamma_i(\mathbf{R}^{-1}\mathbf{r}_i) = \ln \left( \frac{f_{i0}^{[in]}(\mathbf{r}_i)}{f_{i0}^{[in]}(\mathbf{R}^{-1}\mathbf{r}_i)} \right) \equiv H_i(\mathbf{r}_i). \quad (22)$$

For 2D square lattice, the symmetry operator  $R$  is chosen to be 4-fold:

$$R^4 \mathbf{r}_i = \mathbf{r}_i. \quad (23)$$

When we operate  $R$  on the above eq.(22),  $n$  times, we obtain the following relations

$$\begin{aligned} \Delta\gamma_i(\mathbf{r}_i) - \Delta\gamma_i(R^{-1}\mathbf{r}_i) &= H_i(\mathbf{r}_i) \\ \Delta\gamma_i(R\mathbf{r}_i) - \Delta\gamma_i(\mathbf{r}_i) &= H_i(R\mathbf{r}_i) \\ \Delta\gamma_i(R^2\mathbf{r}_i) - \Delta\gamma_i(R\mathbf{r}_i) &= H_i(R^2\mathbf{r}_i) \\ \Delta\gamma_i(R^3\mathbf{r}_i) - \Delta\gamma_i(R^2\mathbf{r}_i) &= H_i(R^3\mathbf{r}_i). \end{aligned} \quad (24)$$

Making use of the definition of  $\gamma_i(\mathbf{r}_i)$  in (7) and the relation (24), one can derive

$$\sum_{m=0}^3 \gamma_i(R^m \mathbf{r}_i) = \sum_{m=0}^3 (\alpha_i(R^m \mathbf{r}_i) - \alpha_i(R^{m+1} \mathbf{r}_i)) = 0. \quad (25)$$

Therefore, it can be shown that

$$\Delta\gamma_i(\mathbf{r}_i) + \Delta\gamma_i(R\mathbf{r}_i) + \Delta\gamma_i(R^2\mathbf{r}_i) + \Delta\gamma_i(R^3\mathbf{r}_i) = 0. \quad (26)$$

We now solve the four unknowns,  $\Delta\gamma(R^m \mathbf{r})$ ,  $m=0 \sim 3$  from eqs.(24) and (26). When we eliminate  $\Delta\gamma(R\mathbf{r})$ ,  $\Delta\gamma(R^2\mathbf{r})$  and  $\Delta\gamma(R^3\mathbf{r})$  from them, we obtain

$$\begin{aligned} \Delta\gamma_i(\mathbf{r}_i) + (\Delta\gamma_i(\mathbf{r}_i) + H_i(R\mathbf{r}_i)) + (\Delta\gamma_i(\mathbf{r}_i) + H_i(R\mathbf{r}_i) + H_i(R^2\mathbf{r}_i)) \\ + (\Delta\gamma_i(\mathbf{r}_i) + H_i(R\mathbf{r}_i) + H_i(R^2\mathbf{r}_i) + H_i(R^3\mathbf{r}_i)) = 0, \end{aligned} \quad (27)$$

which leads to the relation

$$\Delta\gamma_i(\mathbf{r}_i) = -\frac{1}{4}(3H_i(R\mathbf{r}_i) + 2H_i(R^2\mathbf{r}_i) + H_i(R^3\mathbf{r}_i)). \quad (28)$$

Other  $\Delta\gamma_i(R^m \mathbf{r}_i)$  can also be derived straightforwardly from this equation by operating the rotation operator  $R$  repeatedly on the right hand side of (28).

## 5. The NIM

The set of equations in the previous section 4 is solved numerically using the NIM (natural iteration method). When we use the constraint Lagrange multipliers, the NIM consists of the "Major Iteration" and the "Minor Iteration". The major iteration solves the set of basic of equations in (11), the reduction relations in (2) and the normalization relation. It was proved that this iteration always converges from whatever initial guess values it starts with.

The basic expression of the computation is eq.(15) less the normalization factor:

$$g_{ij0}(\mathbf{r}_i, \mathbf{r}'_j) = \exp(-\beta \epsilon_{ij}^0(\mathbf{r}_i, \mathbf{r}'_j) + \frac{\beta}{4}(\mu_i + \mu_j))(f_i(\mathbf{r}_i)f_j(\mathbf{r}'_j))^{3/4} \exp(-\gamma_i(\mathbf{r}_i) - \gamma_j(\mathbf{r}'_j)). \quad (29)$$

Although we work with the pair distribution functions, what we are to solve are essentially the point probability functions  $f_i(\mathbf{r}_i)$ ,  $i=A$  and  $B$ .

(i) Initial guess values: We start with the initial guess values of  $f_i(\mathbf{r}_i)$ . It can be any reasonable function which satisfies essential features of the desired results. In the present case, a Gaussian function with a reasonable constant  $c$  may be used:

$$f_i(\mathbf{r}_i)^{[in]} = \exp(-c\mathbf{r}_i^2). \quad (30)$$

For the initial guess, the normalization of  $f_i(\mathbf{r}_i)^{[in]}$  is not necessary.

(ii) After each major iteration step, we use the output  $f_i(\mathbf{r}_i)^{[out]}$  of the converged minor iterations as the input  $f_i(\mathbf{r}_i)^{[in]}$  for the next major iteration step.

(iii) When  $f_i(\mathbf{r}_i)^{[in]}$  is given, we go to the minor iteration as will be described in the next subsection, to determine the converged value  $\gamma_i(\mathbf{r}_i)^{[out]}$ .

(iv) We then use  $f_i(\mathbf{r}_i)^{[in]}$  and the corresponding  $\gamma_i(\mathbf{r}_i)^{[out]}$  on the right-hand side of (29). Using  $g_{ij0}(\mathbf{r}_i, \mathbf{r}'_j)$  in the normalization relation, the factor  $\exp(\beta\lambda/2)$  can be calculated from

$$\exp\left(\frac{\beta\lambda}{2}\right) = \int d\mathbf{r}_i \int d\mathbf{r}'_j g_{ij0}(\mathbf{r}_i, \mathbf{r}'_j). \quad (31)$$

We multiply this to (29) to derive  $g_{ij}(\mathbf{r}_i, \mathbf{r}'_j)^{[out]}$ .

(v) Use this  $g_{ij}(\mathbf{r}_i, \mathbf{r}'_j)^{[out]}$  in eq.(2) to calculate the output  $f_i(\mathbf{r}_i)^{[out]}$  of this major iteration step:

$$f_i(\mathbf{r}_i)^{[out]} = \frac{1}{2} \sum_{j=1}^2 \int (g_{ij}(\mathbf{r}_i, \mathbf{r}'_j)^{[out]} d\mathbf{r}'_j + g_{ij}(\mathbf{r}'_j, \mathbf{r}_i)^{[out]} d\mathbf{r}'_j). \quad (32)$$

(vi) Use this  $f_i(\mathbf{r}_i)^{[out]}$  in the convergence criterion. One of the possible criteria is

$$\sum_{i=1}^2 \int |f_i(\mathbf{r}_i)^{[out]} - f_i(\mathbf{r}_i)^{[in]}| d\mathbf{r}_i < T_{mjr}, \quad (33)$$

where  $T_{mjr}$  is an appropriate small constant, of the order of  $T_{mjr} = 10^{-5}$ .

(vii) If the criterion is not satisfied, use  $f_i(\mathbf{r}_i)^{[out]}$  of (32) and the corresponding  $\gamma_i(\mathbf{r}_i)^{[out]}$  determined in (iii) as the input  $f_i(\mathbf{r}_i)^{[in]}$  and  $\gamma_i(\mathbf{r}_i)^{[in]}$  for the next major iteration step (iii).

## 6. The Minor Iteration

At each step of the major iteration, we determine the Lagrange multiplier  $\gamma_i(\mathbf{r}_i)$  corresponding to  $f_i(\mathbf{r}_i)^{[in]}$ . This is done numerically as the minor iteration. When the minor iteration has converged, the final output value  $\gamma_i(\mathbf{r}_i)^{[out]}$  is the one corresponding to the given  $f_i(\mathbf{r}_i)^{[in]}$ .

(i) First we calculate  $H_i(\mathbf{r}_i)$  defined in (22) in terms of  $f_{i0}(\mathbf{r}_i)^{[in]}$ , which in turn is calculated in (21) using  $g_{ij0}^{[in]}(\mathbf{r}_i, \mathbf{r}'_j)$  and  $\gamma_i(\mathbf{r}_i)^{[minor in]}$ . In the first step of the minor iteration, one can choose

$$\gamma_i(\mathbf{r}_i)^{[minor in]} = 0. \quad (34)$$

As the major iteration proceeds, we can use the converged value  $\gamma_i(\mathbf{r}_i)^{[out]}$  of the previous minor iteration as the input of the next minor iteration.

(ii) Using  $H_i(\mathbf{r}_i)$  derived in (i), calculate  $\Delta\gamma_i(\mathbf{r}_i)$  in (28).

(iii) Using  $\Delta\gamma_i(\mathbf{r}_i)$  of (ii), derive  $\gamma_i(\mathbf{r}_i)^{[minor\ out]}$  from (18).

(iv) We can use the convergence criterion

$$\sum_{i=1}^2 |\Delta\gamma_i| < T_{mnr}, \quad (35)$$

where  $T_{mnr}$  is also an appropriately chosen small constant, for example  $10^{-5}$ .

(iv) When the major iteration does not satisfy the convergence criterion, use as next, and go back to the step (i)

Although we have a proof that the major iteration always converges, the minor iteration does not necessarily converge. In case where divergence is noticed, we can make the iteration converge by multiplying computed in the step (ii) by a "damping factor"  $\psi$  and use defined below as in (iii)

$$\Delta\gamma_i^{(new)} \leftarrow \psi \Delta\gamma_i^{(ii)}. \quad (36)$$

Usually  $\psi$  is taken to be 0.5, which leads to a rapid convergence.

When we can avoid storing the pair variables  $g_{ij}$  in the memory, we can save the memory space. In the process of calculating the point distribution function  $f_i$ , we may use  $g_{ij}$  but it is not necessary to store  $g_{ij}$  each time.

## 7. Polar coordinates

For 2D alloys, we use the polar coordinates system. For convenience, the polar coordinates are written as

$$\begin{aligned} \rho(m) &\equiv m b & ; & & m=1, 2, \dots, 5 \\ \theta(m;n) &\equiv n \frac{2\pi}{8m} & ; & & n=1, 2, 3, \dots, 8m \end{aligned}$$

By this discretization in the polar coordinates, one can allow an atom to be displaced to one of the 121(=1+8+16+24+32+40) discrete points around each reference lattice point.

## 8. FCC alloys

The continuous CVM can also be applied to an fcc alloy. We use the pair approximation of continuous CVM within the NN pair approximation in the fcc binary alloys. For the binary system, we use the chemical potential to control the composition as was done in the 2-D case. For convenience, we choose

$$\mu_1 = -\mu \quad \text{and} \quad \mu_2 = \mu, \quad (37)$$

so that B atoms increase as  $\mu$  increases. We write the chemical potential terms in the grand potential as

$$-\beta(\mu_1 \rho_1 + \mu_2 \rho_2) = -\frac{\beta}{2} \left( \sum_{i=1}^2 \mu_i \int d\mathbf{r}_i f(\mathbf{r}_i) + \sum_{j=1}^2 \mu_j \int d\mathbf{r}'_j f(\mathbf{r}'_j) \right). \quad (38)$$

The grand potential of the binary FCC alloy system is now given by

$$\begin{aligned}
 \Psi \equiv \frac{\beta\Omega}{N} = & \beta\lambda(1 - \sum_{i=1}^2 \sum_{j=1}^2 \int d\mathbf{r}_i \int d\mathbf{r}'_j g(\mathbf{r}_i; \mathbf{r}'_j) + 6\beta \sum_{i=1}^2 \sum_{j=1}^2 \int d\mathbf{r}_i \int d\mathbf{r}'_j \epsilon(|\mathbf{a} + \mathbf{r}'_j - \mathbf{r}_i|) g(\mathbf{r}_i; \mathbf{r}'_j) \\
 & - \frac{11}{2} \left( \sum_{i=1}^2 \int d\mathbf{r}_i L[f(\mathbf{r}_i)] + \sum_{j=1}^2 \int d\mathbf{r}'_j L[f(\mathbf{r}'_j)] \right) + 6 \sum_{i=1}^2 \sum_{j=1}^2 \int d\mathbf{r}_i \int d\mathbf{r}'_j L[g(\mathbf{r}_i; \mathbf{r}'_j)] - 5 \\
 & - \frac{\beta}{2} \left( \sum_{i=1}^2 \mu_i \int d\mathbf{r}_i f(\mathbf{r}_i) + \sum_{j=1}^2 \mu_j \int d\mathbf{r}'_j f(\mathbf{r}'_j) \right) \\
 & - 6 \sum_{i=1}^2 \sum_{j=1}^2 \int d\mathbf{r}_i \int d\mathbf{r}'_j (A_x(\mathbf{r}_i) + A_x(-\mathbf{r}'_j)) g(\mathbf{r}_i; \mathbf{r}'_j) \\
 & - 6 \sum_{i=1}^2 \sum_{j=1}^2 \int d\mathbf{r}_i \int d\mathbf{r}'_j (A_y(\mathbf{r}_i) + A_y(-\mathbf{r}'_j)) g(\mathbf{r}_i; \mathbf{r}'_j) \\
 & - 6 \sum_{i=1}^2 \sum_{j=1}^2 \int d\mathbf{r}_i \int d\mathbf{r}'_j (A_z(\mathbf{r}_i) + A_z(-\mathbf{r}'_j)) g(\mathbf{r}_i; \mathbf{r}'_j), \tag{39}
 \end{aligned}$$

where  $A_x$ ,  $A_y$  and  $A_z$  are the Lagrange multipliers, and

$$f(\mathbf{r}_i) = \sum_{j=1}^2 \int d\mathbf{r}'_j g(\mathbf{r}_i; \mathbf{r}'_j) \quad ; \quad f(\mathbf{r}'_j) = \sum_{i=1}^2 \int d\mathbf{r}_i g(\mathbf{r}_i; \mathbf{r}'_j). \tag{40}$$

We maximize  $\Psi$  with respect to  $g(\mathbf{r}_i; \mathbf{r}'_j)$ :

$$\begin{aligned}
 \frac{\partial \Psi}{\partial g(\mathbf{r}_i; \mathbf{r}'_j)} = & 6\beta\epsilon(|\mathbf{a} + \mathbf{r}'_j - \mathbf{r}_i|) - \frac{\beta}{2}(\mu_i + \mu_j) - \frac{11}{2} \ln(f_i(\mathbf{r}_i)f(\mathbf{r}'_j)) + 6 \ln(g(\mathbf{r}_i; \mathbf{r}'_j)) - \lambda\beta \\
 & - 6(A_x(\mathbf{r}_i) + A_x(-\mathbf{r}'_j) + (A_y(\mathbf{r}_i) + A_y(-\mathbf{r}'_j)) + (A_z(\mathbf{r}_i) + A_z(-\mathbf{r}'_j))) = 0. \tag{41}
 \end{aligned}$$

The pair distribution functions are then given by

$$\begin{aligned}
 g(\mathbf{r}_i; \mathbf{r}'_j) = & \exp \left( \frac{\lambda\beta}{6} \right) \exp(-\beta\epsilon(|\mathbf{a} + \mathbf{r}'_j - \mathbf{r}_i|) + \frac{\beta}{12} (\mu_i + \mu_j)) (f_i(\mathbf{r}_i)f(\mathbf{r}'_j))^{11/12} \\
 & \times \exp(A_x(\mathbf{r}_i) + A_x(-\mathbf{r}'_j) + (A_y(\mathbf{r}_i) + A_y(-\mathbf{r}'_j)) + (A_z(\mathbf{r}_i) + A_z(-\mathbf{r}'_j))). \tag{42}
 \end{aligned}$$

From eq.(39), we see that when  $\Psi$  is a minimum, we can identify  $\lambda = \frac{\Omega}{N}$ .

## 9. Numerical Examples

We have solved the set of integral equations on the pair distribution functions by discretizing them. This is equivalent to allowing the atomic displacements to finite number of points. When they are discretized, to solve them is a straightforward application of the existing CVM.

The example we have reported previously is on a single component system in a 2-D square lattice [3]. An atomic position  $\mathbf{r}$  is written by the polar coordinates,  $\mathbf{r} = (\rho, \theta)$ . In the discretization, we draw a circle of radius  $\rho = nb$  where  $b$  is a constant and  $n$  takes an integer value. On the  $n$ -th circle, we choose  $8n$  points. Including the origin, the total number of points on and inside the  $n=5$  circle is 121. As for the

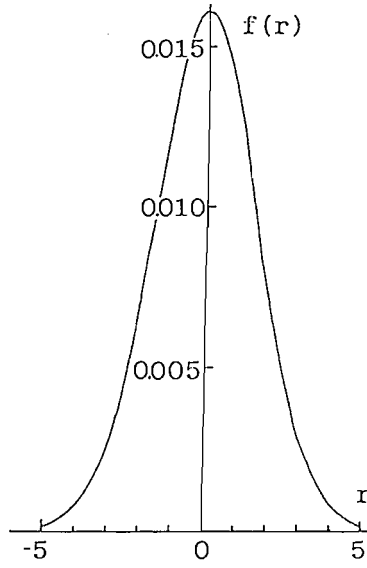


Fig.1 Point distribution function  $f(\rho, \theta=0)$   
 FCC lattice:  $kT/\epsilon_0=0.6$ .

pair variables, we choose the  $\theta_1 = 0$  and  $\theta_2 = 0$  directions pointing to each other so that the inversion symmetry of the right and left displacements can be easily seen. For the interatomic potential energy we use the Lennard-Jones potential:

$$\epsilon(r)/\epsilon_0 = (r_0/r)^{12} - 2(r_0/r)^6 ,$$

whose minimum  $\epsilon(r)=-\epsilon_0$  is at  $r=r_0$ . We choose the radius increment as  $b=0.075r_0$ .

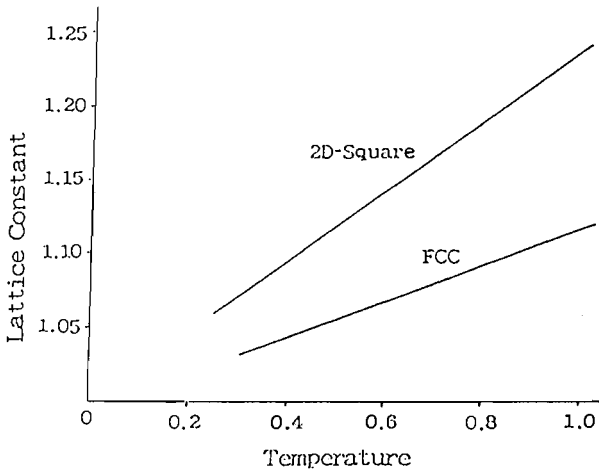


Fig.2 Temperature dependences of  
 lattice constants of 2D and FCC  
 crystals.

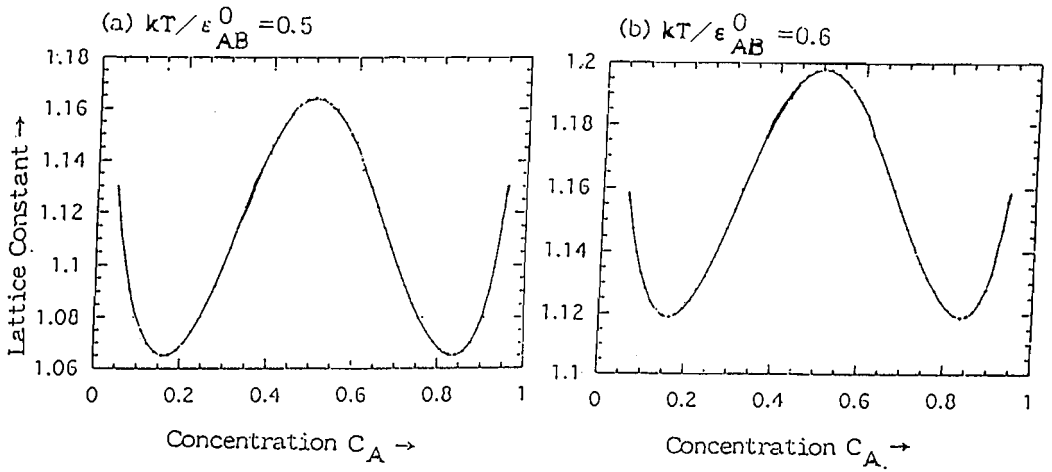


Fig.3 The concentration dependence of 2D binary alloys, with  $\epsilon_{AA}^0 = 0.5 \epsilon_{AB}^0$ ,  $\epsilon_{AA}^0 = 0.7 \epsilon_{AB}^0$ ,  $r_{AA}^0 = 1.1 r_{AB}^0$ , and  $r_{BB}^0 = 1.05 r_{AB}^0$ .

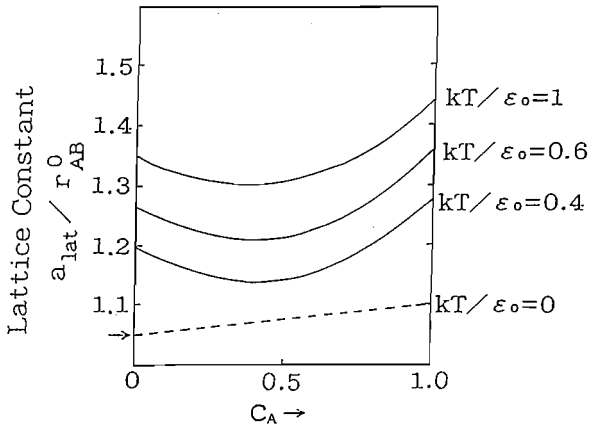


Fig.4 The concentration dependence of 2D binary alloys, with  $\epsilon_{AA}^0 = 0.45 \epsilon_{AB}^0$ ,  $\epsilon_{BB}^0 = 0.45 \epsilon_{AB}^0$ ,  $r_{AA}^0 = r_{AB}^0 = r_{BB}^0$

At each temperature one can determine the equilibrium lattice constant  $a_0$  for the minimum of  $F$ . This leads to the thermal expansion of the alloy lattice. At equilibrium the probability  $f(\rho, \theta=0)$  of finding an atom away from the reference lattice point is of a Gaussian shape, as shown in Fig.1. In Fig.2, we present the temperature dependence of lattice constants of pure 2D square and FCC crystals, calculated by the present continuous displacement treatment of CVM. One can see in Fig.2 that the lattice expansion coefficient of 2D lattice is much larger than that of FCC lattice, with the use of the identical Lennard-Jones (LJ) potential. It is understood that the close packing makes thermal expansion smaller.

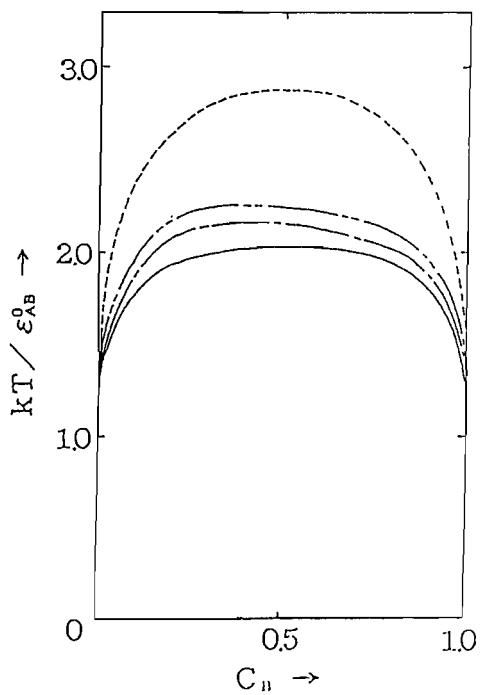


Fig.5 Phase diagrams of 2D binary alloys.

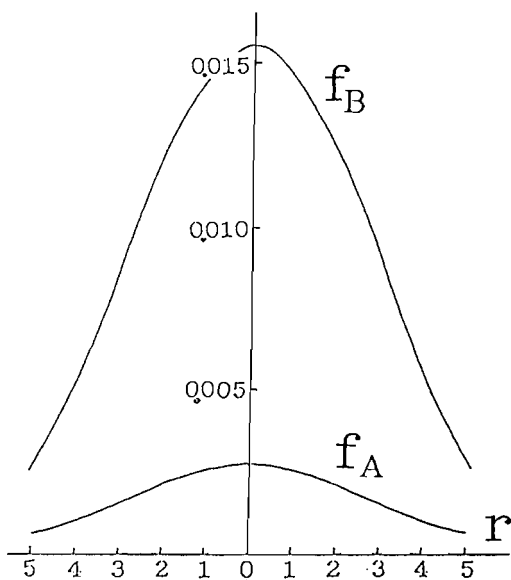


Fig.6 Point distribution functions  $f_A$  and  $f_B$  of binary alloys.  $kT/\epsilon_{AB}=0.6$



In Figs.3 and 4, we show the concentration dependence of the lattice constants of 2D binary alloys. For the calculation of Fig.3, the LJ potential parameters  $\epsilon_{AA}^0 = 0.5 \epsilon_{AB}^0$ ,  $\epsilon_{AA}^0 = 0.7 \epsilon_{AB}^0$ ,  $r_{AA}^0 = 1.1 r_{AB}^0$ , and  $r_{BB}^0 = 1.05 r_{AB}^0$  are used, while  $\epsilon_{AA}^0 = 0.45 \epsilon_{AB}^0$ ,  $\epsilon_{BB}^0 = 0.45 \epsilon_{AB}^0$ ,  $r_{AA}^0 = r_{AB}^0 = r_{BB}^0$  for Fig.4. One can see that the lattice constant of the 2D binary alloys depends sensitively on the choice of the interatomic potentials between the constituent A and B atoms.

The phase diagrams of the 2D binary alloys are shown in Fig.5. In Fig.6, we show the point distribution functions  $f_A$  and  $f_B$  of the binary alloys. The dashed curve in Fig.5 shows the phase separation determined by the conventional CVM with the pair approximation: The parameter  $\epsilon$  is taken such that  $4\epsilon = 2\epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})$ . The solid curve is calculated by using the present continuous CVM, with the LJ parameters of  $\epsilon_{AA}^0 = \epsilon_{BB}^0 = 1.6 \epsilon_{AB}^0$ , and  $r_{AA}^0 = r_{BB}^0 = r_{AB}^0 = 1.0$ . We also present, by dot-dashed and double dot-dashed curves, the phase separation for the LJ parameters of  $\epsilon_{AA}^0 = \epsilon_{BB}^0 = 1.6 \epsilon_{AB}^0$ , and  $r_{AA}^0 = r_{AB}^0$  with  $r_{BB}^0 = 1.05 r_{AB}^0$  and  $= 1.1 r_{AB}^0$ , respectively. Comparing these three phase separation curves, it can be concluded that the effects of local lattice distortion are essentially important in determining the phase stability of binary alloy systems, even for alloys with small size mismatch parameters of the order of  $\sim 2\%$ . The increase in the size mismatch between the constituent atoms raises the temperature of the phase separation: In general, the treatments by the conventional CVM become inaccurate.

In conclusion, we have presented a new formulation of the CVM which allows continuous atomic displacement from lattice point and applied the scheme to the calculations of the phase diagrams of binary alloy systems. For treating 3D systems, the memory space can be reduced by storing only point distribution function  $f(\mathbf{r})$ , but not the pair distribution function  $g(\mathbf{r}, \mathbf{r}')$ . Therefore, continuous CVM scheme can be applicable for the calculations of phase diagrams of 3D alloy systems [6,7], with the use of the standard type of computers.

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# STRUCTURAL STABILITY IN Fe-BASED ALLOYS

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## I. INTRODUCTION

Experimentally it is found that the Fe-Co and Fe-Ni alloys undergo a structural transformation from the bcc structure to the hcp or fcc structures, respectively, with increasing number of valence electrons, while the Fe-Cu alloy is unstable at most concentrations. In addition to this some of the alloy phases show a partial ordering of the constituting atoms. One may wonder if this structural behaviour can be simply understood from a filling of essentially common bands or if the alloying implies a modification of the electronic structure and as a consequence also the structural stability. In this paper we try to answer this question and reproduce the observed structural behaviour by means of accurate alloy theory and total energy calculations.

## II. CALCULATIONS

We have used the basis set of the Linear-Muffin-Tin-Orbital (LMTO) method in the atomic sphere approximation (ASA). The LMTO-ASA is based on the work of Andersen and co-workers<sup>1-4</sup> and the combined technique<sup>5,6</sup> allows us to treat all phases on equal footing. To treat itinerant magnetism we have employed the Vosko-Wilk-Nusair parametrization<sup>7</sup> for the exchange-correlation energy density and potential. In conjunction with this we have treated the alloying effects for random and partially ordered phases with a multisublattice generalization of the coherent potential approximation (CPA).

We have considered the fcc and bcc phases for both random and ordered (partially ordered) alloys. The ordered bcc phase is based on the B2 structure. In this structure only the  $\text{Fe}_{50}\text{X}_{50}$  ( $\text{X} = \text{Co}, \text{Ni}$  or  $\text{Cu}$ ) alloys can be perfectly ordered. For the off-stoichiometry compositions partially ordered alloys have been considered with one

sublattice fully occupied by the atoms with largest concentration and the other sublattice randomly occupied by the remaining atoms. The ordered fcc alloys are based on two different structures; the  $\text{Fe}_{50}\text{X}_{50}$  alloys are based on the CuAu structure ( $\text{L1}_0$ ), while the  $\text{Fe}_{25}\text{X}_{75}$  and the  $\text{Fe}_{75}\text{X}_{25}$  are based on the  $\text{Cu}_3\text{Au}$  structure ( $\text{L1}_2$ ).

To further discuss the underlying mechanisms that forces the phase stabilities we also did calculations where the alloying effects were treated within the so-called virtual crystal approximation (VCA) where the real alloy constituents are replaced by an atom with an average (noninteger) atomic number.

### III. RESULTS

In Fig. 1 the calculated energy of the bcc (fat lines) and fcc (thin lines) phases of the three alloys Fe-Co, Fe-Ni and Fe-Cu are plotted as a function of concentration. All alloys have been treated both in the random (full line) and ordered or partially ordered (dashed line) phases. For the Fe-Co alloy we find, in excellent agreement with experiments, that the ordered bcc phase has the lowest energy up to 85% of Co. At higher Co concentrations experiments say that the hcp random alloy, which is not included in this work, becomes stable. The fcc and hcp structure are always very similar structurally and energetically and the finding of a random fcc phase suggests also that the hcp phase will be lower in energy than the bcc structure. As a matter of fact, in a previous work<sup>8</sup> we found the hcp phase to be stable in this concentration interval. The Fe-Ni system displays many interesting properties and no doubt most of the attention has been focused on the Invar behaviour of this alloy. Another interesting aspect of this alloy is the change of crystal structure from the bcc for the Fe-rich alloys to the fcc for the Ni-rich alloys accompanied by a martensitic transformation. This can also be seen in panel two in Fig. 1. What should be noted here is that we see that the phase transition is at around 45% from the random bcc phase to the ordered fcc phase. This is in good agreement with experiment. If we would not consider ordered alloys we would expect the transition to occur at almost 75% Ni. This means that the partial ordering of the fcc phase plays a crucial role for the structural stability of the Fe-Ni alloys. Finally in panel 3 we display the calculated phase stability of the Fe-Cu alloy. This system can experimentally only be realized for a small amount of Cu. The most interesting effect for this system is whether or not it will stabilize in the ordered phases. The ordering energy is defined as the energy difference between the random alloy and the ordered alloy. For Fe-Cu we find that it is around 150 meV/atom for the bcc alloy with 50% Cu and 260 meV/atom for the fcc alloy at the same concentration. Since alloys which are very stable show partial ordering of the atoms our finding of a big positive value of the ordering energy is consistent with the experimentally found phase separation of the Fe-Cu alloys.

The magnetic moment plays also a very important role for the phase stability in all these systems. The kinks that can be seen in the curves in the concentration region 20 - 50% for all alloys is due to the appearance of a magnetic moment in the fcc phase at these concentrations. The bcc phase is, unlike the fcc phase, magnetic in the whole concentration range. It is first when the fcc phase becomes magnetic that it can compete properly with the bcc phase. The magnetic situation is very intricate especially for the Fe-Ni alloy and was discussed thoroughly by Abrikosov et al.<sup>6</sup>.

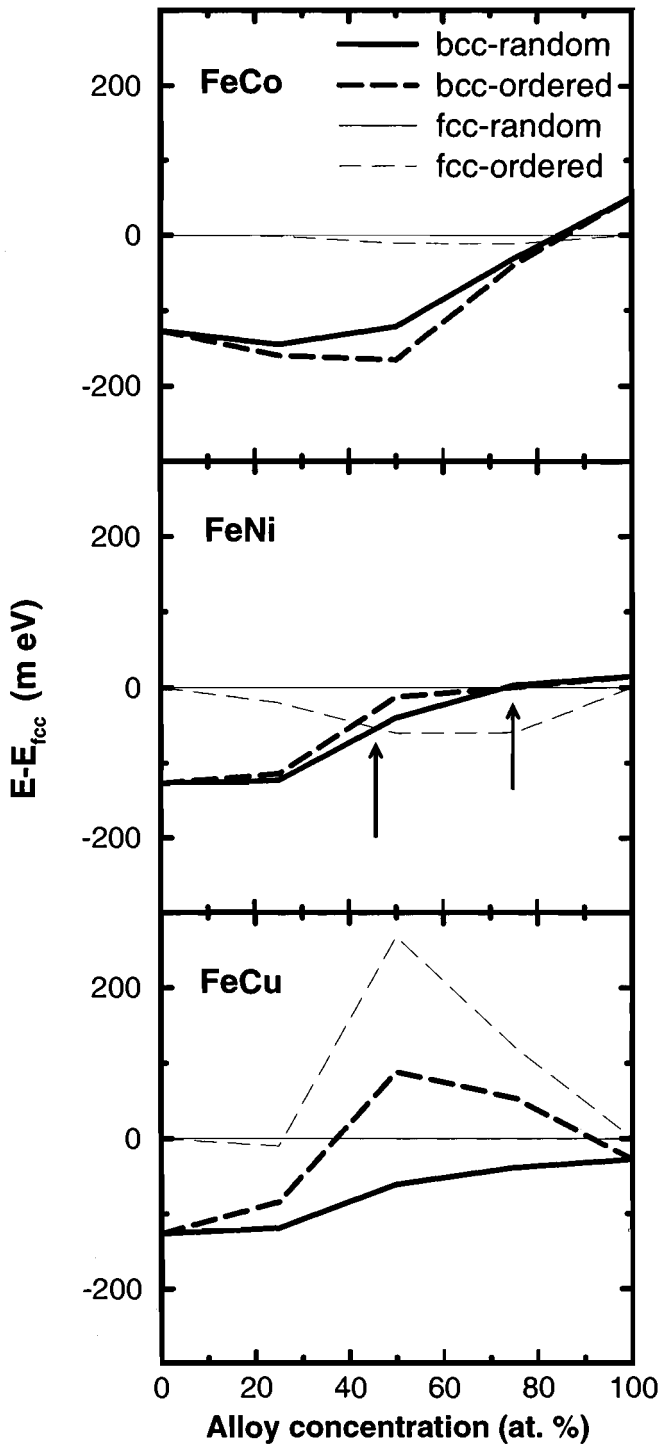


**Figure 1.** The CPA-LSDA-ASA results for the energy of bcc (fat lines) and fcc (thin lines) random and ordered alloys. The fcc random phase is the reference energy and defines zero in the graph. The random phases are given in full drawn lines and the ordered phases are given in dashed lines.

In a previous work<sup>8</sup> we showed that we could reproduce qualitatively the LMTO-CPA results for the Fe-Co system within a simple spin polarized canonical band model. The structural properties of the Fe-Co alloy can thus be explained from the filling of the d-band. In that work<sup>8</sup> we presented the results in canonical units and we could of course not do any quantitative comparisons. To proceed that work we have here done calculations based on the virtual crystal approximation (VCA). In this approximation each atom in the alloy has the same surrounding neighbours, it is thus not possible to distinguish between random and ordered alloys, but one may analyze the energy difference between different crystal structures.

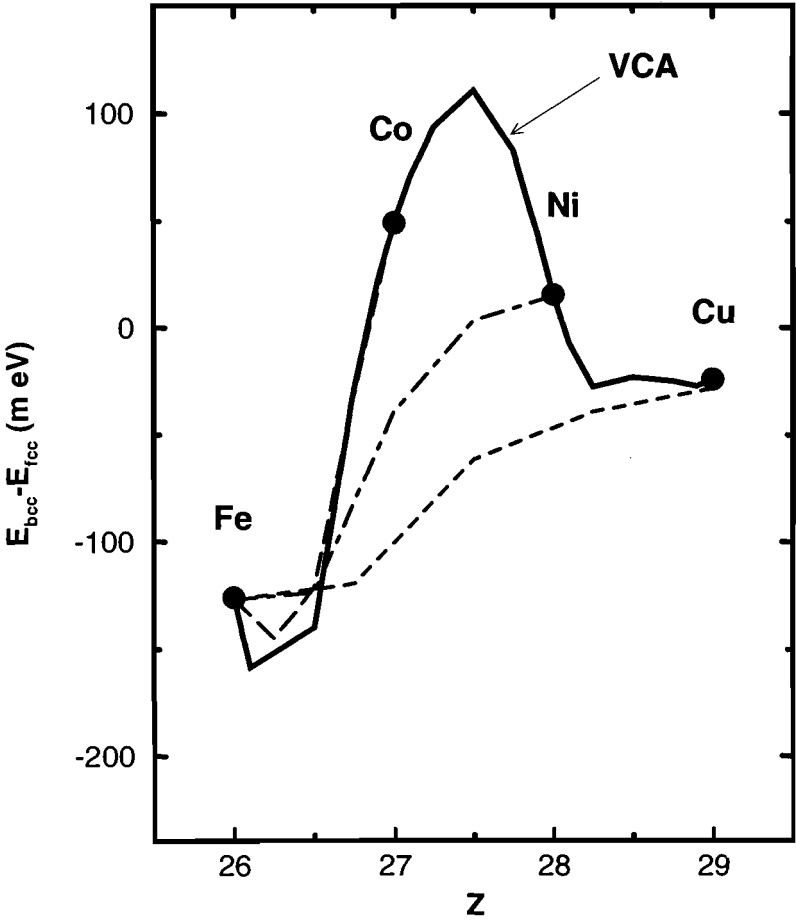


**Figure 2.** Virtual crystal approximation calculations (solid line) compared with coherent potential approximation calculations for Fe-Co (longdashed line), Fe-Ni (dot-dashed line) and Fe-Cu (dashed line). The fcc-bcc energy difference is shown as a function of the atomic number.

In Fig. 2 we show the results of the VCA calculations and the CPA calculations for the three alloys. We have plotted the energy of the bcc structure relative to the energy of the fcc structure as a function of atomic number ( $Z$ ). This means that the bcc structure is stable when we have negative energy values and the fcc structure is stable when we have positive energy values. The simple spin polarized canonical band model shows an excellent qualitative agreement with the VCA calculations. The VCA-calculations in turn show a very good agreement with the CPA-calculations for the Fe-Co alloy, while both for the Fe-Ni and the Fe-Cu alloy the deviation is substantial. Density of states calculations can explain the relative success of the VCA model for the Fe-Co alloy and also its failure for the other two alloy systems. Fe and Co are neighbours in the Periodic Table and the alloy electronic structure exhibits an almost common band behaviour for the spin up band. Due to the large difference in magnetic moment on the Fe and Co sites a split band behaviour occurs for the spin down band, but this split is mainly seen above the Fermi energy. When Fe is alloyed with Ni and Cu this splitting of the bands gets more pronounced and is also seen below the Fermi energy with the result that the VCA model (as well as the spin polarized canonical band model) breaks down for these systems.

#### IV. CONCLUSIONS

To summarize we have reproduced the intricate structural properties of the Fe-Co, Fe-Ni and the Fe-Cu alloys by means of LMTO-ASA-CPA theory. We conclude that the phase diagram of especially the Fe-Ni alloys is heavily influenced by short range order effects. The general trend of a bcc-fcc phase transition at lower Fe concentrations is in accordance with simple band filling effects from canonical band theory. Due to this the structural stability of the Fe-Co alloys may be understood from VCA and canonical band calculations, since the common band model is appropriate below the Fermi energy for this system. However, for the Fe-Ni and the Fe-Cu system this simple picture breaks down.

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# AUGMENTED SPACE RECURSION METHOD FOR THE CALCULATION OF ELECTRONIC STRUCTURE OF RANDOM ALLOYS

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## 1. INTRODUCTION.

Tailoring materials with desirable set of properties for specific applications is one of the important aspects in the present day materials research. Atomistic simulations of physical properties of materials from first principles have become matured with the advent of powerful computers and can be exploited to predict the behaviour of materials without actually synthesizing them. Among the various materials the disordered alloys are used in a variety of applications. The design of alloys to meet specific engineering requirement demands at the microscopic level the first principles electronic structure calculations of these systems. In contrast to the ordered solids, the calculation of most physical properties of disordered alloys require configurational averaging over all realizations of the random variable characterizing the disorder. Among the various methods proposed for this configuration averaging, the most successful and popular method is the coherent potential approximation (CPA). The CPA coupled with the first principles band structure methods in the framework of LDA provides a starting point for the *ab-initio* electronic structure calculation of disordered alloys<sup>1</sup>. Though CPA provides reliable results and useful understanding of various alloy properties but there are many physical situations where the single site approximation inherent in CPA begins to fail. Examples include alloys where clustering become important (in impurity bands of the split band alloys like Zn band in Cu rich CuZn alloys), alloys with short range order (SRO) where the occupation of a particular site is not independent but dictated by its local environment, alloys where there is local lattice distortion because of size mismatch of the constituents leading to off-diagonal disorder. All these phenomena



demands a theory which can take us beyond single site approximation.

Recently we have proposed and implemented a new method<sup>2</sup> for configuration averaging based on Haydock's recursion method<sup>3</sup> and the augmented space theorem of Mookerjee<sup>4</sup>. This method namely the augmented space recursion (ASR) can treat both diagonal and off-diagonal disorder on equal footing and can also take into account the effect of local environment such as SRO<sup>5</sup>. ASR coupled with the tight binding linearized muffin tin orbital method (TB-LMTO)<sup>6</sup> provides a first principles scheme for the description of electronic structure of random alloys. In this communication we shall review the ASR method.

The remainder of this paper is organized as follows: In section 2 we will describe the ASR method. In section 3 we will present the application of ASR to study lattice relaxation effects in CuPd alloys and finally our conclusions.

## 2. THE AUGMENTED SPACE RECURSION

The augmented space formalism (ASF) puts configuration averaging on the same footing as the quantum mechanical averaging by augmenting the Hilbert space spanned by the original Hamiltonian basis set with the configuration space  $\Phi$  spanned by the various allowed configuration states of the random Hamiltonian. The main steps involved in the configuration averaging by ASF are summarized below:

- (a) Let  $\{n_i\}$  be a collection of discrete random variables and  $f(n_1, n_2, \dots)$  be some function of these random variables. Our problem is to compute the expectation or average value of  $f$ ,

$$\langle f \rangle = \int \int \dots \int \prod dn_i f(n_1, n_2, \dots) P(n_1, n_2, \dots)$$

- (b) For a system with uncorrelated disorder the joint probability density  $P(n_1, n_2, \dots)$  may be written as:

$$P(n_1, n_2, \dots) = \prod p_i(n_i)$$

where the independent probability densities  $\{p_i(n_i)\}$  satisfy the property  $p_i(n_i) \geq 0$  and in addition we assume that its moments to all orders are also finite. This allows one to define a self-adjoint operator  $M_i$ , corresponding to each random variable  $n_i$  such that

$$p_i(n_i) = - \left( \frac{1}{\pi} \right) \text{Im} \langle \nu_i^0 | (n_i I - M_i)^{-1} | \nu_i^0 \rangle$$

where  $M_i$  is an operator in the *configuration space*  $\phi_i$  of the variable  $n_i$  spanned by its states  $\{|\nu_i^k\rangle\}$ .  $|\nu_i^0\rangle$  is a specific member of the basis states in  $\phi_i$ . If  $p_i(n_i)$  can be expressed in continued fraction expansion, then the representation of  $M_i$  is a tridiagonal matrix with continued fraction coefficients in diagonal and off diagonal positions.

- (c) The configuration space of the whole set  $\{n_i\}$  is defined as:  $\Phi = \prod^\otimes \phi_i$  and the operator  $\tilde{M}^{(i)} = I \otimes I \otimes \dots \otimes M_i \otimes \dots \otimes I$ . Further the *ground state*  $|\nu^0\rangle$  in  $\Phi$  is

defined as  $|\nu^0\rangle = |\nu_1^0\rangle \otimes |\nu_2^0\rangle \dots$  which is a subspace of  $\Phi$ . With the aid of little algebra we can easily verify:

$$|\nu_0\rangle = \prod_{\lambda_i} (\sum \sqrt{p_{\lambda_i}} |\lambda_i\rangle)$$

where  $|\lambda_i\rangle$  are the eigen-states of  $\tilde{M}^i$  and  $\{p_{\lambda_i}\}$  are the associated probability weights. The augmented space theorem then states that

$$\langle f \rangle = \langle \nu^0 | \tilde{f}(\tilde{M}^1, \tilde{M}^2, \dots) | \nu^0 \rangle$$

where  $\tilde{f}$  is the same function of  $\tilde{M}^{(i)}$  as  $f$  was of the  $n_i$ 's. This expresses the expectation value of  $f$  in terms of fixed non-random quantities.

- (d) The same theorem may be extended to correlated disorder. Now the joint probability density is expressed as :

$$P(n_1, n_2, n_3 \dots) = p_1(n_1) p_2(n_2 | n_1) p_3(n_3 | n_2, n_1) \dots$$

An operator  $\tilde{M}_c^{(i)}$  is constructed such that

$$\tilde{M}_c^{(i)} = \sum \dots \sum_{k_{i-1}} P_1^{k_1} \otimes P_2^{k_2} \otimes \dots \otimes M_i^{k_1 \dots k_{i-1}} \otimes I$$

where the operator  $M_i^{k_1 \dots k_{i-1}}$  is associated with the conditional probability density  $p_i(n_i | n_1, n_2, n_3 \dots)$  and  $P_i^{k_i}$  are projection operators on a specific state  $k_i$ . For the purpose of configuration averaging the previous theorem for uncorrelated disorder still holds good with  $\tilde{M}^{(i)}$  replaced by  $\tilde{M}_c^{(i)}$ .

For the electronic structure calculations in a disordered system,  $f$  is chosen to be the Green function  $(zI - H(\{n_i\}))^{-1}$  where  $H$  is the Hamiltonian of the system and  $n_i$  are the random site occupation variables. According to ASF configuration averaged density of states (DOS) is given by:

$$\langle \rho(E) \rangle = -1/\pi \text{Im} \{ \langle \Psi_0 | (E\tilde{I} - \tilde{H})^{-1} | \Psi_0 \rangle \}$$

where  $\tilde{H}$  is the Hamiltonian defined in the augmented space  $\Psi = H \otimes \phi$ . We note that both correlated and un-correlated disorder can now be treated on equal footing.

For the description of the random Hamiltonian we employ TB-LMTO formalism in the most tight binding representation<sup>6</sup>. The Hamiltonian for the binary random alloy takes the form:

$$H_{RL,R'L'}^{\beta(alloy)} = \hat{C}_{RL}^{\beta} \delta_{RR'} \delta_{LL'} + (\hat{\Delta}_{RL}^{\beta})^{1/2} S_{RL,R'L'}^{\beta} (\hat{\Delta}_{R'L'}^{\beta})^{1/2} \quad (1)$$

where  $\hat{C}_{RL} = C_{RL}^A n_R + C_{RL}^B (1 - n_R)$ ;  $\hat{\Delta}_{RL}^{1/2} = (\Delta_{RL}^A)^{1/2} n_R + (\Delta_{RL}^B)^{1/2} (1 - n_R)$ .  $C_{RL}^A$ ,  $C_{RL}^B$ ,  $\Delta_{RL}^A$  and  $\Delta_{RL}^B$  are the potential parameters of the constituents A and B of the alloy,  $S_{RL,R'L'}^{\beta}$  is the structure matrix in the most localized representation,  $n_R$  are local site-occupation variables which randomly takes value 1 or 0 according to whether the site is occupied by an atom of type A or not, with probabilities proportional to the concentrations of the constituents. According to the prescription of the augmented space formalism, the effective non-random Hamiltonian  $\tilde{H}$  in augmented space is then

constructed from the random Hamiltonian  $H_{RL,R'L'}^{\alpha(alloy)}$  by replacing the random variable  $\{n_R\}$  by the corresponding self-adjoint operators  $\{\hat{M}_R\}$ . Once the effective Hamiltonian has been set in , the recursion method provides an efficient algorithm for calculating diagonal matrix element of the resolvent or Green function associated with the effective Hamiltonian  $\tilde{H}$ . Given the starting vector

$$|\Psi_0\rangle = |i, \nu_0\rangle$$

in the augmented space one generates a discrete chain of vectors  $|\Psi_i\rangle$  by the following three term recursion relation:

$$\tilde{H}|\Psi_i\rangle = a_i|\Psi_i\rangle + b_{i+1}|\Psi_{i+1}\rangle + b_i|\Psi_{i-1}\rangle$$

This prescription transforms the effective Hamiltonian to a tridiagonal form and thus leads directly to a continued fraction representation for the configuration averaged Green function matrix element  $\langle\Psi_0|G|\Psi_0\rangle = [G_{ii}]_{av}$ . This algorithm is usually continued to a finite number of steps and finally appended with a suitable terminator.

The numerical implementation of ASR have been discussed in details in previous communications<sup>2,5</sup> and here we shall present only its salient points. A state vector in the augmented space contains information of both the original Hilbert space of the Hamiltonian as well as the configuration space. The basis vectors defined in the configuration space carries the information of the occupation variable at each site. It is a string of zeros and ones and can be stored in binary words and logical operations can be used to describe the action of the Hamiltonian in the configuration space. This procedure is analogous to the multi-spin coding method used to study Ising model. Further the symmetry of the full Hamiltonian in the augmented space is exploited to reduce its rank. The use of symmetry as well as multi-spin coding not only reduces the memory of computation but also makes the computation much faster. Further this method has recently been made fully charge self consistent within LDA. We will now present one application of the ASR method to an alloy system where there is strong off-diagonal disorder.

### 3. LATTICE RELAXATION EFFECTS IN CuPd

CuPd is an important alloy system where there is appreciable mismatch between the atomic radii of the constituents. This non-isochoricity results in local lattice distortion, ie., an appreciable expansion of the lattice around the Pd atom in Cu-rich CuPd alloys. In addition to the usual substitutional disorder in a random binary alloy, this lattice relaxation effect introduces positional disorder. This positional disorder gets reflected in the structure matrix of the TB-LMTO Hamiltonian leading to a complicated off-diagonal disorder. So the study of alloys with local lattice distortion requires a configuration averaging method which can treat both diagonal as well as off-diagonal disorder.

In order to study lattice relaxation effect by ASR we assume a simple model. As a first step we consider the terminal point approximation. Here the distortion of the lattice taken into account is the stretching or the contraction and angular distortion of the bond connecting two sites in a lattice and the effect of neighbouring site is neglected. As a result of such distortion the structure matrix takes the form:

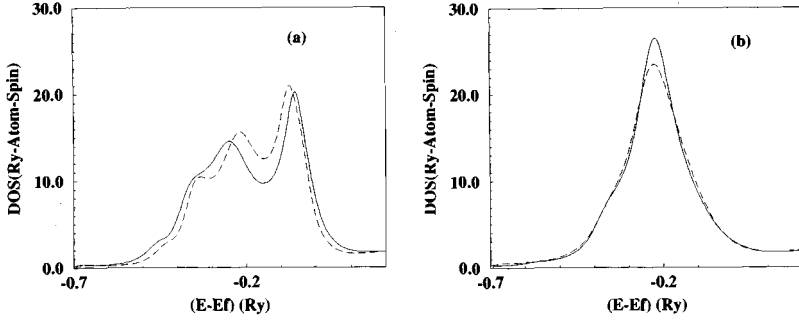


Figure 1: The local DOS for  $\text{Cu}_{75}\text{Pd}_{25}$  alloys. The solid line represents the result without lattice relaxation and the dashed with lattice relaxation. (a) at the Pd site (b) at the Cu site. Energies have been measured from the Fermi energy  $E_f$

$$S_{iL,jL'}^\beta = S_{iL,jL'}^{\beta(AA)} n_i n_j + S_{iL,jL'}^{\beta(AB)} (n_i(1 - n_j) + n_j(1 - n_i)) + S_{iL,jL'}^{\beta(BB)} (1 - n_j)(1 - n_i)$$

The amount of lattice relaxation in our calculation is decided by the rigid ion structure model (RIS). According to RIS the lattice relaxes in such a way so as to keep all the nearest-neighbour interatomic distances close to the sum of corresponding atomic radii. For CuPd this model slightly overestimates the degree of relaxation. Within these approximation we compute the configuration averaged local density of states for  $\text{Cu}_{75}\text{Pd}_{25}$  random alloys by the ASR method discussed earlier. The calculated local density of states at the Pd and the Cu sites with and without lattice relaxation effect is presented in Fig.1(a) and Fig.1(b) respectively. In Fig.1(a) we find that at the Pd site due to lattice relaxation effect there is suppression of the low energy peak as well as narrowing of the DOS in comparison to the case where lattice relaxation effect is not taken into account. The latter effect is due to the lattice expansion around the Pd atom. Further at the Cu site there is very little change in DOS between the relaxed and the un-relaxed lattice. These results agree quite well with the experiments of Wright *et. al.*<sup>7</sup>. (A detailed comparison of the DOS with other theoretical studies is presented by Saha and Mookerjee<sup>8</sup>)

In conclusion we propose ASR as an efficient computational scheme to study electronic structure of random alloys which allows us to take into account the coherent scattering from more than one site. Consequently ASR can treat effects such as SRO and essential off-diagonal disorder due to lattice distortion arising out of size mismatch of the constituents.

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# THE VIENNA AB-INITIO SIMULATION PROGRAM VASP: AN EFFICIENT AND VERSATILE TOOL FOR STUDYING THE STRUCTURAL, DYNAMIC, AND ELECTRONIC PROPERTIES OF MATERIALS

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## 1. INTRODUCTION

For more than thirty years the local-density-approximation (LDA) [1] has formed the basis of the progress towards an *ab-initio* description of complex processes in materials. A remarkable step on this way was realized eleven years ago when Car and Parrinello (CP) [2] pointed out that the ionic and electronic degrees of freedom of a system need not to be treated separately, but may be optimized simultaneously. The work of Car and Parrinello has triggered many fruitful developments and today we are able to treat systems and processes on the basis of fully quantum-mechanical simulations that are far more complex than has been thought to be possible before. However, especially for metals, some serious difficulties remain: (a) The original CP approach is based on a coupled pseudo-Newtonian dynamics for the ionic coordinates and for the electronic wavefunctions and requires a careful control of the adiabaticity of the system. In practice it turns out that adiabaticity can be maintained only if the ionic and electronic subsystems are effectively decoupled because the existence of an energy-gap at the Fermi-level leads to largely different time-scales for electronic and ionic excitations. For metals adiabaticity must be enforced, e.g. by draining the kinetic energy transferred from the ions to the electrons via a Nosé thermostat attached to the electrons (the energy lost by the ions must then be restored by a second thermostat) [3]. (b) Most CP-programs are based on plane-wave (PW) basis-sets. This allows to take advantage of the highly efficient fast-Fourier-transform (FFT) technology for calculating the operation of the Hamiltonian on a wavefunction and avoids the appearance of Pulay-terms in the calculation of the Hellmann-Feynman forces acting

on the atoms. PW basis-sets can be used only in conjunction with a pseudopotential-description of the electron-ion interaction. Still, with conventional pseudopotentials the convergence of the PW-expansion is slow, especially for transition-metals and for first-row elements. (c) The calculation of the Kohn-Sham orbitals necessitates explicit orthonormalizations - these operations scale with the third power of the number of valence-electrons ( $O(N^3)$ -scaling) and hence rapidly determine the computational effort for large systems.

In this paper we describe the *Vienna ab-initio simulation program* VASP [4, 5, 6] which was developed with the aim of bringing an efficient solution to these problems: (a) The problem of adiabaticity is eliminated altogether by calculating the electronic ground-state exactly after each ionic move. This can be achieved either via a global minimization of the Kohn-Sham (KS) total energy or via an iterative calculation of the occupied and some of the lowest unoccupied eigenstates of the KS Hamiltonian (combined in an outer iteration-loop with an effective charge-density-mixing algorithm). A brief description and an estimation of the comparative efficiency of different techniques will be given in Sec. 2.3. (b) The electron-ion interaction is described by ultrasoft pseudopotentials which allow to optimize at the same time PW-convergence and transferability (see Sec. 2.1). (c) The impact of the  $O(N^3)$  orthonormalization operations is minimized by choosing an appropriate strategy for the calculation of the KS-ground-state. We find that this is more easily achieved with iterative diagonalizations of the KS-Hamiltonian than with global minimization methods. (d) To achieve energy-conservation during the MD simulation it is necessary to use finite-temperature density-functional theory [7] where the electronic free energy is the conserved quantity. In addition, the broadening of the one-electron energy-levels leads to a faster convergence of Brillouin-zone integrations.

We shall first review the basic principles of VASP and then describe exemplary applications to alloys and compounds: (a) the calculation of the elastic and dynamic properties of a metallic compound ( $\text{CoSi}_2$ ), (b) the surface reconstruction of a semi-conducting compound ( $\text{SiC}$ ), and (c) the calculation of the structural and electronic properties of  $\text{K}_x\text{Sb}_{1-x}$  Zintl-phases in the liquid state.

## 2. TECHNICAL ASPECTS OF AB-INITIO MOLECULAR-DYNAMICS, ESPECIALLY FOR METALS

### 2.1 Ultrasoft pseudopotentials

Ultrasoft pseudopotentials have been introduced with the aim of optimizing simultaneously PW-convergence and transferability [8, 9]. Fast convergence is achieved by decomposing the charge-density  $\rho(\vec{r})$  into a smooth part described in terms of pseudo-orbitals  $\Phi_n(\vec{r})$  and localized augmentation charges

$$\rho(\vec{r}) = \sum_n f_n |\Phi_n(\vec{r})|^2 + \sum_n \langle \phi_n | \beta_j \rangle \langle \beta_i | \Phi_n \rangle Q_{ij}(\vec{r})$$

where  $f_n$  is the occupancy of state  $n$ , the  $\beta_i$ 's are localized projection states determining the nonlocal part of the pseudopotential according to

$$V_{NL} = \sum_{ij} D_{ij}^{\text{ion}} |\beta_j\rangle \langle \beta_i| ,$$

and the  $Q_{ij}(\vec{r})$  are localized augmentation functions. The indices  $i$  and  $j$  are a compact notation for the quantum numbers and reference energies for the valence states. By using more than one reference energy one can achieve a high accuracy of the pseudopotential over very large energy ranges and hence optimal transferability. The price to pay is that the pseudo-orbitals now satisfy a generalized orthonormality constraint

$$\langle \Phi_n | \mathbf{S} | \Phi_n \rangle = \delta_{nm}$$

with the overlap matrix  $\mathbf{S}$  defined as

$$\mathbf{S} = 1 + \sum_{ij} q_{ij} | \beta_j \rangle \langle \beta_i |$$

where the  $q_{ij} = \int Q_{ij}(\vec{r}) d^3r$  are the augmentation charges. The  $\Phi_n$ 's also obey a generalized KS equation.

Ultrasoft pseudopotentials have now been constructed for all elements for all elements from H to Bi [10]. It has been shown that without any loss of accuracy even for first-row and transition-elements small PW basis-sets comparable in size to those necessary for soft normconserving pseudopotentials for Al or Si can be used. For any further details, see [9, 37].

## 2.2 Finite-temperature LDA and $\vec{k}$ -space integration

It has been shown [12, 13] that for metals energy-conservation along the MD-trajectory can be achieved only within the finite-temperature LDA formalism of Mermin [7]. At finite T the conserved quantity is the electronic free energy which is variational with respect to the charge-density  $\rho(\vec{r})$ , the orbital occupancy  $f_n$ , and the chemical potential  $\mu(\vec{r})$ . The FT-LDA formalism also puts the "smearing" methods introduced earlier with the aim of improving the convergence of Brillouin-zone integrations on a firm footing [14, 15]. Within VASP a variety of these techniques best adapted for different applications has been implemented. For dynamical simulations the Methfessel-Paxton [16] technique based on a set of special  $\vec{k}$ -points is the method of choice because it allows to calculate the Hellmann-Feynman forces directly as the derivatives of the free energy. For a comparative discussion of the relative merits of other approaches we refer to the recent paper by Kresse and Furthmüller [17].

## 2.3 Determination of the LDA ground-state

For the calculation of the LDA ground-state one can proceed either via the "direct" methods, i.e. via the global minimization of the total free energy with respect to the electronic degrees of freedom, or via the diagonalization (for large PW basis-sets necessarily iterative diagonalization) of the KS Hamiltonian in combination with an iterative update of charge-density and potential.

**2.3.1 Direct minimization of the total energy.** A variety of minimization techniques have been proposed and implemented for *ab-initio* -MD simulations: (a) steepest-descent algorithms [18], (b) damped second-order equations-of-motion (EOM) [19], and (c) conjugate-gradient (CG) schemes [20, 21, 22]. The CG approach applied to all bands simultaneously (CGa) is parameter-free and normally as efficient as the second-order EOM, but requires the explicit orthonormalization of the conjugate gradient to all lower-lying bands. Hence this approach involves a large number of  $O(N^3)$



operations. A possible way to eliminate this difficulty is to generalize the KS functional to non-orthogonal orbitals [23, 24]. Here we shall not discuss any technical details (we refer to [17]), but we will present below detailed comparisons of the performance of CGa algorithms as compared to iterative diagonalization strategies.

**2.3.2 Iterative matrix diagonalization.** An important point to realize is that with PW basis-sets the dimension of the Hamiltonian matrix is typically of the order  $N_{atom} \times 100$ , whereas only  $2 \times N_{elect}$  (i.e. typically 10 percent) eigenstates are occupied by electrons. Hence iterative techniques for the calculation of the lowest eigenstates are infinitely more advantageous than a complete diagonalization. During the development of VASP [4, 5, 6] a variety of different techniques for the iterative diagonalization of the KS Hamiltonian have been tested. The most efficient methods are (a) the sequential (i.e. band-by-band) CG algorithms originally proposed by Teter et al. [20] for total-energy minimization and later used by Bylander et al. [25] for the iterative calculation of the one-electron energies and (b) a novel variant of the residual-vector minimization method (RMM) first proposed by Wood and Zunger[27] on the basis of the direct inversion in the iterative subspace developed by Pulay [26].

*Band-by-band conjugate-gradient (CG) techniques.* The sequential CG technique minimizes the Rayleigh quotient

$$\epsilon_{app} = \frac{\langle \Phi_m | \mathbf{H} | \Phi_m \rangle}{\langle \Phi_m | \mathbf{S} | \Phi_m \rangle}$$

for an approximate eigenstate  $|\Phi_m\rangle$ . Variation of the Rayleigh quotient with respect to  $|\Phi_m\rangle$  yields the residual vector

$$|R(\Phi_m)\rangle = (\mathbf{H} - \epsilon_{app}\mathbf{S}) |\Phi_m\rangle$$

which must be zero for the exact eigenstate. Orthonormality of the eigenstates requires the gradient to be orthogonal to all other eigenvectors, convergence is improved by introducing a preconditioning function  $\mathbf{K}$  to damp the corrections for the large-wavevector components. Hence minimization is performed along the gradient vector

$$|g(\Phi_m)\rangle = (1 - \sum_n |\Phi_n\rangle\langle\Phi_n| \mathbf{S}) \mathbf{K} (\mathbf{H} - \epsilon_{app}\mathbf{S}) |\Phi_m\rangle \quad ,$$

respectively the conjugate gradient vector (for details, see [17, 28]). In addition, for metals a diagonalization in the subspace spanned by the  $|\Phi_m\rangle$  (subspace rotation) must be performed. The main drawback of the otherwise highly efficient sequential CG algorithm is the need for the explicit orthonormalization of the gradients which not only introduces a large number of  $O(N^3)$  operations, but also requires a large band-width of the communication between the main memory and the CPU. For both reasons, the efficiency decreases for larger systems.

*Residual minimization method (RMM-DIIS).* Wood and Zunger [27] proposed to minimize the norm of the residual vector instead of the Rayleigh quotient. This is an unconstrained minimization condition. Each minimization step starts with the evaluation of the preconditioned residual vector  $\mathbf{K} |R(\Phi_m^i)\rangle$  for the approximate eigenstate  $|\Phi_m^i\rangle$ . Then the norm of the residual vector is minimized in the subspace spanned by  $|\Phi_m^i\rangle$  and the new trial eigenstate is given by

$$|\Phi_m^{i+1}\rangle = |\Phi_m^i\rangle + \lambda \mathbf{K} |R(\Phi_m^i)\rangle \quad .$$

Assuming the linearity of the residual vector, this is equivalent to the minimization of the quantity

$$\frac{\sum_{ij} \alpha_i^* \alpha_j \langle R(\Phi_m^i) | R(\Phi_m^j) \rangle}{\sum_{ij} \alpha_i^* \alpha_j \langle \Phi_m^i | \mathbf{S} | \Phi_m^j \rangle}$$

and hence this step is often referred to as the direction inversion in the iterative subspace (DIIS). The DIIS essentially represents a technique for accelerating the convergence of the minimization and a corrector step preventing the residual minimization of converging to the wrong eigenvalue. For technical details, see [17, 28]. However, the RMM-DIIS minimization can be quite ill-conditioned when there are closely-spaced eigenvalues. This problem can be solved by performing a subspace-rotation after each update of a complete set of bands. After the subspace-rotation the residual vectors are orthonormal to the current set of trial eigenvectors,

$$\langle \Phi_n | R(\Phi_m) \rangle = 0, \quad \forall m, n$$

and convergence to the "wrong" eigenvalue is effectively suppressed. Still, the initialization of the RMM-DIIS iterations must be performed with great care to ensure convergence to the real ground state. In problematic cases, the sequential CG scheme can be used for the first few iterations before switching to the RMM-DIIS.

**2.3.3 Mixing** The iterative diagonalization techniques require the update of the charge-density and of the potential after performing a full loop over all bands. Especially for large cells, this must be done with great care to avoid serious charge-sloshing problems. We have implemented an optimized strategy for charge-density-mixing based on the residuum of the input-charge-density  $\rho_{in}$  defined as ( $\rho_{out}$  is the output-charge-density)

$$R[\rho_{in}] = \rho_{out}[\rho_{in}] - \rho_{in} \quad .$$

If we assume that the residuum may be linearized around the selfconsistent charge-density  $\rho_{sc}$ , i.e.

$$R[\rho] = -\mathbf{J}(\rho - \rho_{sc}) \quad ,$$

than the convergence depends on the eigenvalue spectrum of the Jacobian matrix  $\mathbf{J}$ . Vanderbilt and Louie [29] have shown that  $\mathbf{J}$  is related to the susceptibility  $\chi$  of the system through  $\mathbf{J} = 1 - \chi \mathbf{U}$  where  $\mathbf{U}$  is the operator describing the change of the potential induced by a change in the charge density. Hence an efficient mixing strategy must aim at constructing a good approximation to  $\mathbf{J}$ . For VASP, Kresse and Furthmüller [28] have developed an optimized Pulay-type [26] mixing scheme based on the minimization of the charge-density residuum, involving an update of the current approximation to  $\mathbf{J}$  (which plays the role of a preconditioning matrix) at any step. For all technical details and for the relation to other mixing techniques, we refer to their paper.

**2.3.4 The complete algorithm.** A complete selfconsistency loop in VASP consists of the following steps:

- (1) Subspace rotation.
- (2) RMM-DIIS or CG minimization to get the  $N_{band} > 2 \times N_{elect}$  lowest eigenvalues.
- (3) Gram-Schmidt orthogonalization (for RMM-DIIS) only).
- (4) Update of Fermi-energy and partial occupancies, charge density mixing.

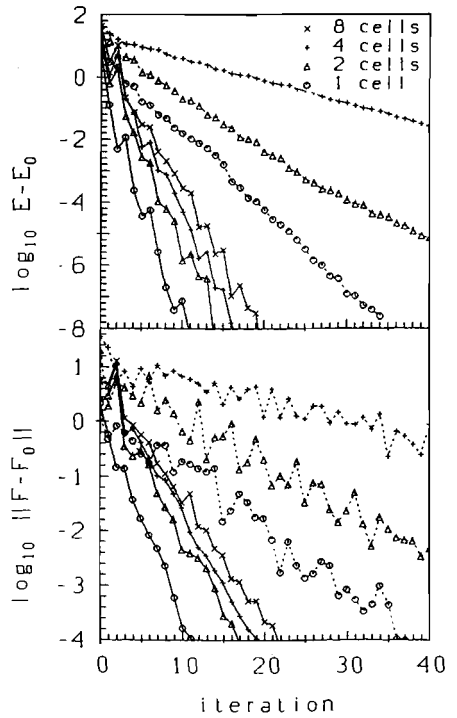
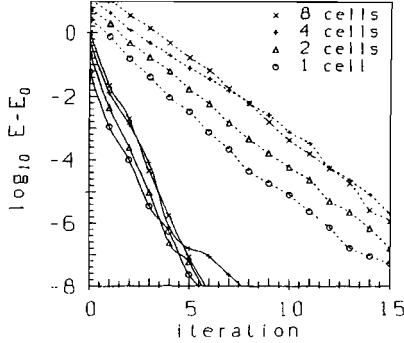


Figure 1: Convergence of the total energy and of the Hellmann-Feynman forces for ensembles of paramagnetic Fe atoms with 4 to 32 atoms. Part (a) shows the results of non-selfconsistent calculations performed with a fixed potential, part (b) the results of selfconsistent calculations. Full lines represent the RMM-DIIS (iterative diagonalization) results, broken lines the CGa (total-energy minimization) calculations. Cf. text.

Remarks: (a) It is essential that the subspace-rotation be performed between the mixing-step and the iterative diagonalization. This is the reason for separating orthogonalization and subspace-rotation. Even with this arrangement, the fraction of  $O(N^3)$  operations remains small. (b) The Gram-Schmidt orthogonalization may be performed efficiently using a scheme based on a Choleski decomposition of the overlap matrix  $\mathbf{S}$ . (c) Convergence is always slowest for the highest eigenvalues. Hence for metals it is essential to include a sufficient number of empty bands (i.e.  $N_{band} > N_{elect}/2$ ).

To illustrate the performance and stability of VASP, we show in Fig. 1 the convergence of the total energy and of the Hellmann-Feynman forces as obtained with the RMM-DIIS algorithm and with a CGa minimization of the total energy at the example of paramagnetic Fe-ensembles with an increasing number of atoms. The atomic positions are those of a fcc lattice, randomized by adding arbitrary displacement vectors measuring 5 % of the lattice constant. The cells are arranged linearly - this is the worst possible case for charge-sloshing. An ultrasoft pseudopotential with a cut-off energy of 240 eV was used. For the smallest system Brillouin-zone integrations were based on a  $4 \times 4 \times 4$  grid of special points and the Methfessel-Paxton method with a broadening of  $\sigma = 0.3$  eV. For the larger ensembles the number of  $\vec{k}$ -points was decreased proportionally (see also Table I). To achieve reasonable convergence it is necessary to

Table 1: Time per iteration (in seconds) for the RMM-DIIS and CGa algorithms applied to Fe-ensembles with  $N_{atom}$  atoms and using  $N_{kpoints}$   $\vec{k}$ -points for Brillouin-zone integrations. The calculations performed at the  $\Gamma$ -point only where performed with a version of the code using real wave-functions.

| $N_{atom}$ | $N_{elect}$ | $N_{kpoints}$ | RMM-DIIS | CGa  |
|------------|-------------|---------------|----------|------|
| 4          | 32          | 32            | 21.0     | 16.0 |
| 8          | 64          | 16            | 39.0     | 32.0 |
| 16         | 128         | 8             | 80.0     | 65.0 |
| 32         | 256         | 2             | 92.0     |      |
|            |             | 1             | 27.0     |      |
| 108        | 864         | 1             | 360.0    |      |

include  $1.5 \times N_{atom}$  empty bands. The calculation was started with a random initialization of the wavefunctions. Part (a) compares the convergence of a non-selfconsistent calculations performed with a fixed potential using the RMM-DIIS iterative method and the CGa total-energy minimization. The important point to note is that for both techniques convergence is essentially independent of the system-size, and that the CGa method needs about twice as many iteration steps. Part (b) compares the results of the selfconsistent calculations. Here charge-sloshing is the main problem. Still, for the RMM-DIIS+mixing method, the difference between the smallest and the largest cell is only a factor of two. This is in direct contradiction to the predictions by Annett [30] of a quadratic scaling of the number of iterations with the largest linear dimension. The reasons for the much better performance are first that the Pulay mixing is quadratically convergent and second that a special "preconditioning" of the charge-density residuum effectively eliminates the problems arising from the quadratic divergence in the Hartree term of the potential. In the CGa technique, massive charge-sloshing problems are evident. For this reason we recommend to use CGa approaches only for semiconducting systems. The sequential CG scheme is also useful for semiconductors and metals, but the RMM-DIIS algorithm usually performs better because it needs a smaller number of iterations (see Kresse and Furthmüller [17, 28] for more detailed tests).

In addition, one has off course to consider the CPU time. Table I gives the time necessary to perform one iteration for the various Fe-ensembles on an IBM-RISC6000/590 workstation (a single-processor CRAY-C90 is about four times faster). In addition to the 4 to 32 atom cells we give the results for a  $3 \times 3 \times 3$  supercell with 108 atoms where only the  $\Gamma$  point of the Brillouin-zone has been used. We find that for  $N_{elect} \leq 1000$  the scaling is better than quadratic, for small systems ( $N_{elect} \leq 300$ ) and  $N_{kpoints} \times N_{elect} = \text{const.}$  the scaling is even almost linear. For small systems, the CGa approach requires slightly less CPU time per iteration (but at least two times as many iterations, see Fig. 1), for larger system the scaling is much less favourable because of the larger number of orthonormalizations.

Given the efficiency of VASP, electronic structure calculations with or without a static optimization of the atomic structure can now be performed on fast workstations for systems with a few hundred inequivalent atoms per cell (including transition-metals and first row elements). Molecular dynamics simulations extending over several picoseconds are feasible (at tolerable computational effort) for systems with 1000 or more valence electrons. As an example we refer to the recent work on the metal/nonmetal transition in expanded fluid mercury[31].

### 3. APPLICATIONS OF VASP TO ALLOYS AND COMPOUNDS

In the following we review very briefly applications of VASP to alloys and inter-metallic compounds illustrating the potential in making ab-initio predictions of materials properties, in characterizing solid surfaces, and in studying the structure and properties of complex melts. For a more extensive list of applications, see Refs. [10, 17].

#### 3.1 The cohesive, elastic, and dynamic properties of cobalt-disilicide

CoSi<sub>2</sub> is a material of high technological interest because of potential applications as a structural material (due to its low specific weight and excellent oxidation behaviour) and for microelectronic devices (semiconductor/conductor interfaces may be manufactured in a controlled way by heteroepitaxial growth of metallic CoSi<sub>2</sub> films on Si substrates). Very recently VASP has been used to calculate the cohesive, elastic, and dynamic properties of CoSi<sub>2</sub>. In addition the cohesive and elastic properties have also been calculated using the all-electron full-potential linearized augmented plane-wave (FLAPW) method in order to provide a stringent test of the accuracy of the pseudopotential and the completeness of the plane-wave basis set[32]. In the VASP calculations, Co and Si were described by ultrasoft pseudopotentials with cut-off radii of 2.7 a.u. and 2.5 a.u., respectively, allowing for an energy-cutoff of 200 eV. In both VASP and FLAPW calculations the Hedin-Lundqvist[33] form of the LDA functional was used, using VASP also nonlocal generalized gradient corrections (GGC's) to the LDA functional according to Becke and Perdew[34] have been considered. In both calculations Brillouin-zone integrations using the Methfessel-Paxton technique[16] were performed for  $\vec{k}$ -points sets large enough to achieve convergence to within 1 to 2 % compared to the results extrapolated to an infinite number of  $\vec{k}$ -points.

Using VASP the elastic constants  $B = (C_{11} + 2C_{12})/3$ ,  $C' = (C_{11} - C_{12})/2$  and  $C_{44}$  have been calculated as (a) the second derivatives of the total energy density with respect to compressive, tetragonal, and rhombohedral lattice strains (and allowing for the relaxation of all internal degrees of freedom), (b) the first derivatives of the components of the stress tensor with respect to the strain, and (c) as the first derivatives of the phonon dispersion relations  $\omega(\vec{q})$  along high-symmetry directions at the  $\Gamma$  point. The phonon dispersion calculations have been calculated using the *ab-initio* force-constant approach based on large supercells[35]. For CoSi<sub>2</sub>, a tetragonal supercell with 36 atoms has been used to calculate the phonon dispersion relations along the (100) directions, similar set-ups have been used for the other symmetry directions. Using FLAPW, the elastic constants can be calculated only via route (a).

The results given in Table II can be summarized as follows: (a) Ultrasoft pseudopotentials allow to achieve perfect agreement with all-electron calculations even for very modest cutoff-energies. (b) The use of the LDA leads to the well-known over-binding effect (too small lattice parameters, overestimated binding energy and lattice-stiffness). LDA elastic constants calculated at the experimental lattice parameter are in good agreement with experiment. For the case of CoSi<sub>2</sub> the GGC's correct for the overbinding and lead to quasi-perfect agreement with the experimental data for the cohesive and elastic properties. (c) Second derivatives of the total energy and the stress-strain relation lead to elastic constants in perfect agreement. Somewhat larger discrepancies appear along the phonon-route. This shows that although our supercells are large enough to predict accurate phonon frequencies in almost the entire Brillouin zone (for a detailed comparison with experiment see Stadler et al. [32]), even larger cells will be required for phonons with very large wavelengths.

Table 2: Lattice parameter  $a_0$  (in Å) and elastic constants  $B$ ,  $C_{11}$ ,  $C_{12}$ , and  $C_{44}$  for CoSi<sub>2</sub> (in GPa), calculated using all-electron (FLAPW) and pseudopotential (VASP) techniques in the LDA and using GGC corrections.

|                         |     |           | $a_0$             | $B$       | $C_{11}$  | $C_{12}$  | $C_{44}$ |
|-------------------------|-----|-----------|-------------------|-----------|-----------|-----------|----------|
| FLAPW                   | LDA | $E_{tot}$ | 5.292             | 201.8     | 273.3     | 166.0     | 97.4     |
|                         |     |           | exp. <sup>a</sup> | 171.4     | 233.8     | 140.2     |          |
| VASP                    | LDA | $E_{tot}$ | 5.283             | 200.2     | 273.1     | 163.7     | 100.6    |
|                         |     |           | exp. <sup>a</sup> | 168.1     | 227.6     | 138.4     | 93.6     |
|                         |     | stress    |                   | 199.1     | 236.4     | 162.9     | 100.3    |
|                         |     | phonon    |                   | 172.4     | 236.4     | 140.4     | 97.7     |
| VASP                    | GGC | $E_{tot}$ | 5.350             | 173.1     | 225.0     | 147.2     | 85.7     |
| Experiment <sup>b</sup> |     |           | 5.365             | 171.5±3.4 | 224.7±4.4 | 144.9±3.9 | 85.0±1.1 |

<sup>a</sup> Elastic constants calculated and the experimental lattice constant.

<sup>b</sup> Experimental data from Ref. [36].

### 3.2 Reconstruction of silicon-carbide surfaces

Recently there has been a growing interest in the use of wide-gap semiconductors such as diamond and silicon carbide in high-power and high-temperature microelectronics. One of the basic requirements for the development of a C- or SiC-based device technology is the possibility of a controlled homo- and heteroepitaxial growth of thin films via chemical vapour deposition or molecular beam techniques. Progress in these technologies necessitates a detailed knowledge of the structural and electronic properties of the growth surfaces. Both the clean and the hydrogenated low-index surfaces of diamond have been thoroughly studied using VASP[37, 38, 39]. The case of SiC is more complex because more than two hundred long-range ordered polytypes are known. Many of them have been well investigated using *ab-initio* techniques[40, 41], but only a small number of studies of the surface properties are known[42, 43].

The simplest polytype assume the zinc-blende structure, 3C, with Si and C planes alternating in the (001) direction. For 3C-SiC(001) the  $p(2 \times 1)$  and  $c(2 \times 1)$  surfaces have been studied in detail by dynamical low-energy-electron diffraction (LEED)[44, 45] and *ab-initio* calculations using VASP[43, 46, 47]. The  $c(2 \times 2)$  surface is usually assumed to be carbon-terminated, but two completely different reconstructions have been proposed: (a) Double-bonded carbon dimers arranged as staggered rows  $>C=C<$  bridges between alternating pairs of Si surface-atoms (see Fig. 2(a))[45]. (b) Staggered rows of C<sub>2</sub> groups (with triple C≡C bonds) in Si bridging sites (see Fig. 2(b))[44]. Recently Käckell et al.[46] have studied the stability of both models using VASP. C has been described by an ultrasoft pseudopotential with a cutoff-energy of 240 eV (see Furthmüller et al.[37]), Si by a normconserving pseudopotential. For model (a) the relaxation of the atomic geometry yields a dimer-length of  $d_{C-C} = 1.38$  Å (i.e. very close to that of a C-C double bond in a hydrocarbon molecule), and an inward-relaxation of the C top-layer by 0.29 Å. For model (b) the bond-length within the C<sub>2</sub> groups is  $d_{C-C} = 1.23$  Å (corresponding to a triple-bond), the C top-layer relaxes outward by 0.24 Å, Si atoms not connected by C<sub>2</sub>-bridges form dimers with a bond-length of  $d_{Si-Si} = 2.38$  Å. Energetically, both surfaces are nearly degenerate, with model (b) only a few meV/surface-atom lower in energy. Surface states within the

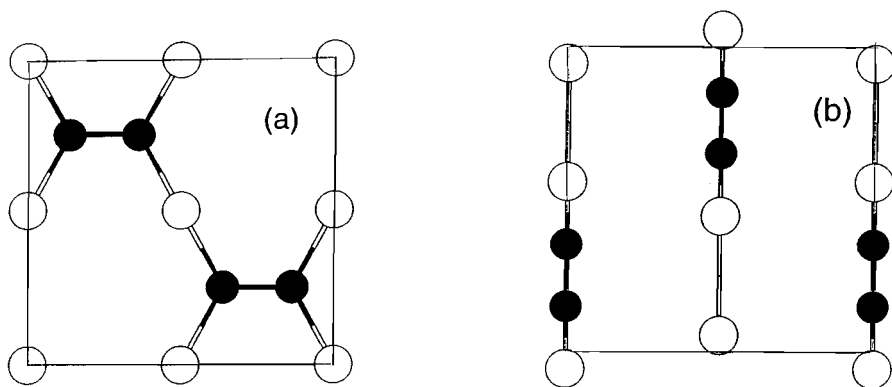


Figure 2: Models for the carbon-terminated  $3\text{C-SiC}(001)c(2\times 2)$  surface: (a) staggered  $\text{C}=\text{C}$ -dimer model, (b)  $\text{C}_2$  groups in Si bridge sites. Cf. text.

bulk gap are predicted for the staggered dimer model (a), but not for the  $\text{C}_2$ -bridge model (b). Recent photoemission data have not detected any surface states in the gap, thus confirming the preference for model (b). VASP has also been used to study hydrogenated of the C-terminated surface, as well as Si-terminated surfaces of various stoichiometries[43, 46, 47].

### 3.3 The structural and electronic properties of K-Sb Zintl phases in the crystalline and molten states

The "Zintl"-phases formed by the alkali-metals and B-group metals or semi-metals from groups III to VI occupy a fascinating niche in the physics and chemistry of intermetallic compounds, because they display a wide variety of chemical bonding and electronic properties. Because of the large electronegativity difference one expects that the alkali atoms transfer their single valence electron to the electronegative element and the most stable compound is expected for the stoichiometric composition at which the octet-rule is satisfied. For the I-V compounds this leads to  $\text{I}_3\text{V}$ -compounds with a salt-like crystal structure ( $\text{BiLi}_3$ - or  $\text{AsNa}_3$ -type). In addition, at the equiatomic composition polyanionic compounds with a covalent character are formed: after charge-transfer, the  $\text{V}^-$ -ions are isoelectronic to the chalcogen-atoms and form, according to the "Zintl-principle" infinite  $\text{V}_\infty^-$  spiral chains in analogy to the spiral crystal structures of the chalcogen-elements ( $\text{NaP}$ - and  $\text{LiAs}$ -type, see e.g. von Schnering et al. [48]). Note that both types of compounds are non-metallic, with an "ionic" gap in the octet-compounds separating the highest occupied anion-band from the lowest empty cation-band and a "covalent" gap in the polyanionic compounds separating anion-states that are bonding and anti-bonding along the spiral chains[49]. Many experiments show that the characteristic physical anomalies do not disappear on melting and suggest that the local order in the melt might be very similar to that in the corresponding crystalline compounds - in particular the existence of covalently bonded Sb-chains in liquid alkali-Sb alloys has been suggested on the basis of neutron-scattering experiments[50]. To confirm such a suggestion by detailed *ab-initio* molecular-dynamics simulations remains a challenging task, both because of the complexity of the interatomic interactions and the time required to reach local chemical equilibrium.

Here we present first results of *ab-initio* LDA-MD studies of crystalline and liquid K-Sb alloys[51]. The liquid alloys are modelled by 64-atom ensembles of appropriate

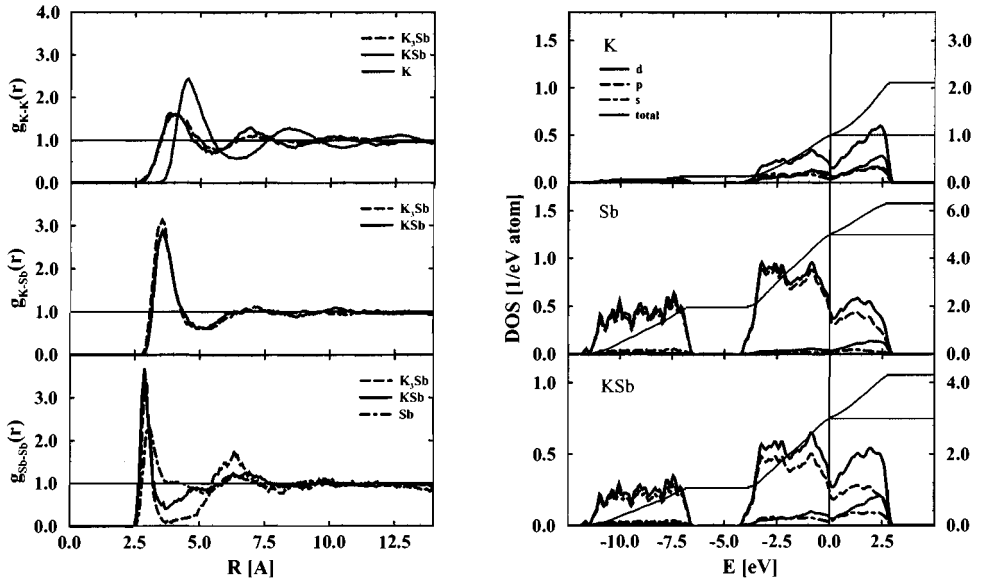


Figure 3: (a) Partial pair correlation functions  $g_{ij}(R)$  in liquid K-Sb alloys. (b) Total, partial, and local electronic densities of states in liquid  $K_{0.50}Sb_{0.50}$ . Cf. text.

composition, the dynamical simulations are performed in a canonical ensemble with a Nosé-thermostat, using a time-increment of 3 fs (with the exact LDA ground-state and Hellmann-Feynman forces calculated after each MD-step). A characteristic property of the Zintl-compounds is the large negative excess-volume which is not known very accurately for the liquid alloys. First, we determined the zero-pressure density at each composition by a series of short constant-volume MD runs. At the equilibrium density, at each composition MD runs over about 10 ps where performed (for details we refer to the work on pure liquid Sb [52]). Fig. 3(a) summarizes the results for the atomic structure. The partial pair correlation functions show that the dominant features of the liquid structure are: (a) A strong tendency to heterocoordination of the Sb-ions with short K-Sb distances, almos. no direct Sb-Sb neighbours at the octet-composition  $K_3Sb$ , and a Sb-Sb coordination number of  $N_{Sb-Sb} \sim 2$  at the equiatomic composition. (b) Together with strong, short Sb-Sb bonds this confirms the existence of broken and entangled Sb-Sb chains in the liquid alloys.

Further confirmation of this picture comes from the electronic structure. Fig. 3(b) demonstrates that the characteristic features of the crystalline band-structure are preserved in the liquid phase <sup>1</sup>: The valence band is split into a low-lying Sb-s band of one-dimensional character and bonding and non-bonding ( $pp\sigma$ ) bands just below the Fermi level. The Fermi-energy falls into a "pseudo-gap" between the non-bonding and the anti-bonding ( $pp\sigma$ ) bands - the crystalline KSb compound is semiconductor with a narrow gap of 0.7 eV (we only note in passing that the VASP results for the crystalline compounds are in perfect agreement with the earlier all-electron calculations[49]). The existence of a pseudogap for the liquid alloys explains the electronic transport anomalies observed at this composition[54]. The close similarity of the electronic structure

<sup>1</sup>The local and partial densities of state have been calculated using projections of the plane-wave components of the eigenstates onto spherical waves centred at the atomic sites[53].



of crystalline and molten KSb with that of crystalline and liquid Se is a very striking illustration of the validity of the "Zintl-principle".

## 4. CONCLUSIONS

In this article we have reviewed very briefly the basic ingredients that make the *Vienna ab-initio simulation program* VASP a technique of choice for studying the properties of and complex processes in materials: (a) The use of ultrasoft pseudopotentials allows to treat transition-metals and first-row elements at a computational effort that is not much bigger than for simple metals and semiconductors. (b) The exact calculation of the LDA ground-state after each ionic move eliminates all non-adiabaticity problems - this is especially important for systems close to a metal/nonmetal transition. (c) The impact of the cumbersome orthogonalization operations on the scaling of the computational effort with the number of electrons is minimized by using iterative diagonalization via the residual-minimization-method RMM, together with optimized mixing procedures, for the calculation of the ground state. (d) Finite-temperature LDA helps to improve energy-conservation and to speed-up the convergence of Brillouin-zone integrations.

The performance of VASP for alloys and compounds has been illustrated at three examples: The calculation of the properties of cobalt disilicide demonstrates that even for a transition-metal compound perfect agreement with all-electron calculations may be achieved at much lower computational effort, and that elastic and dynamic properties may be predicted accurately even for metallic systems with rather long-range interactions. Applications to surface-problems have been described at the example of the 3C-SiC(100) surface. Surface physics and catalysis will be a particularly important field for the application of VASP, recent work extends to processes as complex as the adsorption of thiopene molecules on the surface of transition-metal sulfides[55]. Finally, the efficiency of VASP for studying complex melts has been illustrate for crystalline and molten Zintl-phases of alkali-group V alloys.

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# Configurational Kinetics Studied by PPM

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## 1. Introduction

As is well recognized, various macroscopic properties such as mechanical properties are controlled by microstructure, and the stability of a phase which consists of each microstructure is essentially the subject of electronic structure calculation and statistical mechanics of atomic configuration. The main subject focused in this article is configurational thermodynamics and kinetics in the *atomic* level, but we start with a brief review of the stability of *microstructure*, which also poses the configurational problem in the different hierarchy of scale.

Transmission electron microscopic observation reveals various morphologies of precipitates depending upon the constituents and composition of an alloy system, history of heat treatments etc. Typical examples are spherical precipitates found in Ni-Cr-Al system and cuboidal precipitates in Fe-Mo system [1]. The first question raised is what determines the shape of a precipitate.

A theoretical framework for this problem was provided by Nabarro [2] nearly half century ago. In his celebrated work, he calculated strain energy,  $E_{strain}$ , of an ellipsoid as a function of  $c/a$  ratio where  $a$  and  $c$  are, respectively, the major and minor axes of an ellipsoid. He demonstrated that a spherical precipitate induces highest strain energy while a minimum energy is realized by a plate like precipitate. Under a constant volume, however, the total surface area is smallest for a sphere. Eventually a balance between the surface energy,  $E_{surface}$ , and elastic strain energy,  $E_{strain}$ , determines an optimum shape of the precipitate, which may claim the minimization of the total energy of the system

$$E_{total} = E_{strain} + E_{surface}. \quad (1)$$

It is realized that Nabarro's theory deals with a single precipitate in the matrix and interactions among precipitates are not considered. Therefore, the configurational problem i.e. an alignment of precipitates are beyond the scope of the theory. The most striking phenomenon which manifests the interactions among precipitates is the particle *splitting* observed for  $\gamma'$  precipitates of Ni-Al system by Miyazaki et al [3] about a decade ago. Opposite to well known coarsening phenomenon, a precipitate splits into several pieces. Such is a typical example dictating the importance of the elastic interaction among particles which overcomes the increase of surface energy. Theoretical studies including computer

simulation have been advanced mainly by Khachaturyan and his coworkers [4], and they revealed various roles played by elastic interactions among precipitates.

It is emphasized that configuration of microstructure is essentially the subject of energetics. The optimization of various elastic energy contributions dominate a whole realm. The stable configuration and evolution kinetics in the microstructural level are, therefore, controlled and determined through variational process operated on the total energy including elastic interaction energy,  $E_{int}$ ,

$$E_{total} = E_{strain} + E_{surface} + E_{int}. \quad (2)$$

Contrary to the *microstructural* level, the entropy plays a significant role in the stability and kinetics of *atomic* level which is the main concern of this article. Among potential theoretical tools, Cluster Variation Method (hereafter CVM) [5] has been recognized as one of the most efficient ways of evaluating and incorporating entropy contribution. In fact, once the analytical expression of the free energy functional based on the CVM entropy formula is obtained, one can derive various thermodynamic quantities such as a phase diagram, instability (Spinodal ordering ) temperature [6], short range order diffuse intensity spectrum [7, 8] from a single free energy formula in a consistent manner [9]. Recent progress of electronic structure calculation even enables us to perform a first-principles calculation of the phase stability.

Path Probability Method (hereafter PPM) [10, 11, 12, 13] is recognized as a kinetic version of the CVM, namely the extension of the variational principle into the time-space coordinate. Hence, various fruitful features are inherited from the CVM. Among them is the capability of incorporating wide range of atomic correlations associated with phase transitions, and the ordering and disordering kinetics which claim spatially extended atomic correlations are studied with sufficient accuracy. A noticeable feature of the PPM is the fact that state variables (cluster probabilities or correlation functions of the CVM) and their time derivatives are not explicitly dealt, which is in marked difference with other kinetic theories. Also, the fact that relevant quantities derived for the long time limit correctly converge to the equilibrium ones predicted by the CVM ensures the reliability of the PPM. Hence the combination of the CVM and PPM provides invaluable tool to study thermodynamic properties of a given system starting from non-equilibrium to equilibrium states. In the present article, the main subject is the *atomic configurational kinetics* studied by the PPM.

It should be realized that unlike the study of equilibrium thermodynamics for which a model is often mapped onto Ising system, elementary mechanism of atomic motion plays a deterministic role in the kinetic study. In an actual alloy system, diffusion of an atomic species is mainly driven by vacancy mechanism. The incorporation of the vacancy mechanism into PPM formalism, however, is not readily achieved, since the abundant freedom of microscopic path of atomic movement demands intractable number of variational parameters. The present study is, therefore, limited to a simple *spin* kinetics, known as Glauber dynamics [14] for which flipping events at fixed lattice points drive the phase transition. Hence, the present study for a spin system is regarded as a precursor to an alloy kinetics. The limitation of the model is critically examined and pointed out in the subsequent sections.

Since a considerable amount of review articles on both theoretical frameworks and calculated results have been reported[15-25], the main objective of the present study is placed on the comparisons with experimental results. The organization of the present report is as follows: In the next section, for the sake of completeness, a brief theoretical description of the PPM is summarized from the previous articles. In the third section, *disorder-L1<sub>0</sub>* transition is focused and visualized atomic (spin) configuration is compared with recent high resolution electron micrograph. In the fourth section, ordering relaxation

in a single phase field of  $L1_0$  and  $L1_2$  phases are studied. The derived long range order parameters are converted into the electrical resistivity change and compared with recent experimental measurements.

## 2. Path Probability Method

In the CVM, the free energy of a given alloy is approximated in terms of probabilities for a selected set of finite clusters. The largest cluster explicitly considered in the free energy functional specifies the level of the approximation. The common practice for an fcc-based system is the tetrahedron approximation [26] in which nearest neighbor tetrahedron cluster is taken as the largest cluster. Hence, within the tetrahedron approximation, the free energy expression,  $F$ , is symbolically expressed as

$$F = F \left( T, \{x_i^\delta\}, \{y_{ij}^{\delta\delta'}\}, \{z_{ijk}^{\delta\delta'\delta''}\}, \{w_{ijkl}^{\delta\delta'\delta''\delta'''}\} \right), \quad (3)$$

where  $i, j, k, l$  indicate atomic species (up and down spins), and  $x_i^\delta, y_{ij}^{\delta\delta'}, z_{ijk}^{\delta\delta'\delta''}$  and  $w_{ijkl}^{\delta\delta'\delta''\delta'''}$  represent, respectively, the cluster probability of atomic configuration specified by subscript(s) on a point, nearest neighbor pair, nearest neighbor triangle and nearest neighbor tetrahedron clusters located on the sublattice designated by superscript(s). Note that all the cluster probabilities are not independent but are interrelated each other through geometric relationships such as

$$x_i^\delta = \sum_{\delta'} \sum_j y_{ij}^{\delta\delta'} = \sum_{\delta'\delta''} \sum_{jk} z_{ijk}^{\delta\delta'\delta''} = \sum_{\delta'\delta''\delta'''} \sum_{jkl} w_{ijkl}^{\delta\delta'\delta''\delta'''} \quad (4)$$

It is remembered that atomic correlation generally exceeds the range of atomic interaction. Hence, in constructing a free energy formula, it is necessary to limit the range of atomic interaction within the spatial extension of the largest cluster assumed in the entropy term  $S$ . In the present study, we adopt nearest neighbor pair interaction model for an internal energy term  $E$ . The free energy is, therefore, given as

$$\begin{aligned} F &= E - TS \\ &= \frac{1}{2} \omega \sum_{\delta\delta'} \frac{N_2^{\delta\delta'}}{6} \sum_{ij} e_{ij} y_{ij}^{\delta\delta'} \\ &\quad - T \left[ - \left( \frac{5}{4} \right) \sum_{\delta} N_1^{\delta} \sum_i L(x_i^{\delta}) + \sum_{\delta\delta'} N_2^{\delta\delta'} \sum_{ij} L(y_{ij}^{\delta\delta'}) - 2 \sum_{ijkl} L(w_{ijkl}^{\delta\delta'\delta''\delta'''}) \right], \quad (5) \end{aligned}$$

where  $\omega$  is the coordination number,  $e_{ij}$  is the nearest neighbor interaction energy between  $i$  and  $j$  species,  $L(z)$  represents  $z \ln z - z$ ,  $N_1^{\delta}$  and  $N_2^{\delta\delta'}$  are determined by the symmetry of the phase. It is readily shown that, for  $L1_0$  ordered phase,  $N_1^{\alpha} = N_1^{\beta} = 2$ ,  $N_2^{\alpha\alpha} = N_2^{\beta\beta} = 1$  and  $N_2^{\alpha\beta} = 4$ , and for  $L1_2$  ordered phase  $N_1^{\alpha} = 1$ ,  $N_1^{\beta} = 3$ ,  $N_2^{\alpha\beta} = N_2^{\beta\beta} = 3$  and  $N_2^{\alpha\alpha} = 0$ . For the disordered phase, since the distinction of the sublattices vanishes the summation operations with respect to  $\delta$  and  $\delta'$  are eliminated and  $N_1 (= N_1^{\delta}) = 4$  and  $N_2 (= N_2^{\delta\delta'}) = 6$  are input. Minimization of the free energies under the constraint,

$$\sum_{ijkl} w_{ijkl}^{\delta\delta'\delta''\delta'''} = 1, \quad (6)$$

followed by the common tangent construction (or an equivalent method) determines the phase equilibria among the three phases. The calculated *disorder*- $L1_0$ - $L1_2$  phase diagram is shown in Fig. 1. It is noted that the effective nearest neighbor pair interaction energy  $v_2$  is related to the pair interaction energies  $\{e_{ij}\}$  through

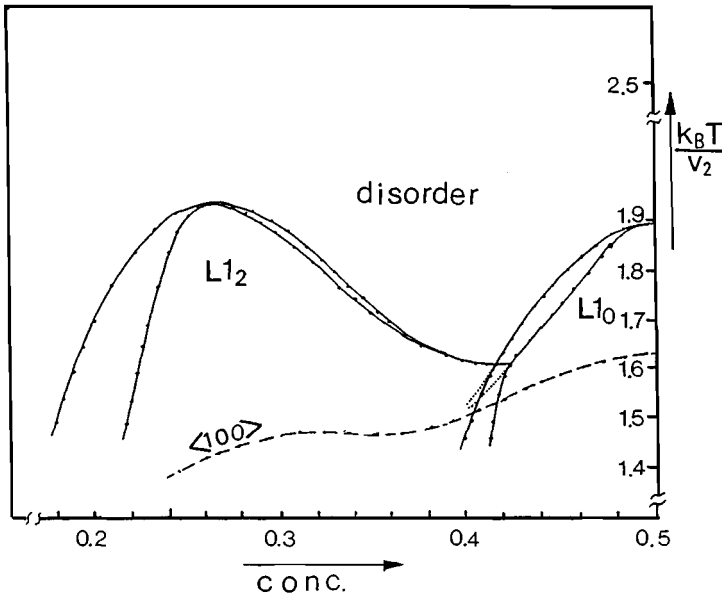


Figure 1: Disorder- $L_{10}$ - $L_{12}$  phase diagram [9]. The broken line indicates the  $\langle 100 \rangle$  Spinodal ordering locus and dotted lines the metastable phase boundaries. The temperature axis is normalized with respect to the nearest neighbor pair interaction energy. The ordering transition temperatures of  $L_{10}$  and  $L_{12}$  phases are  $\sim 1.89$  and  $\sim 1.92$ , respectively.

$$v_2 = \frac{1}{2} \{ (e_{ii} + e_{jj}) - 2e_{ij} \} \quad (7)$$

by which the temperature axis in Fig. 1 is normalized.

For the PPM, corresponding to the free energy of the CVM is the *Path Probability Function* (hereafter *PPF*),  $P(t; t + \Delta t)$ , which is an explicit function of time and is defined as the product of three factors  $P_1$ ,  $P_2$  and  $P_3$ . Each factor is provided in the following in the logarithmic expression.

$$\ln P_1 = \left( \frac{1}{4} \right) \sum_{\delta} N_1^{\delta} \left\{ (X_{1,2}^{\delta} + X_{2,1}^{\delta}) \ln(\theta \Delta t) + (X_{1,1}^{\delta} + X_{2,2}^{\delta}) \ln(1 - \theta \Delta t) \right\}, \quad (8)$$

$$\ln P_2 = -\frac{\Delta E}{2k_B T}, \quad (9)$$

and

$$\begin{aligned} \ln P_3 = & -\left( \frac{5}{4} \right) \sum_{\delta} N_1^{\delta} \left\{ \sum_{i,j} L(X_{i,j}^{\delta}) - \sum_i L(x_i^{\delta}(t)) \right\} \\ & + \sum_{\delta\delta'} N_2^{\delta\delta'} \left\{ \sum_{ij,kl} L(Y_{ij,kl}^{\delta\delta'}) - \sum_{ij} L(y_{ij}^{\delta\delta'}(t)) \right\} \\ & - 2 \left\{ \sum_{ijkl,mnop} L(W_{ijkl,mnop}) - \sum_{ijkl} L(w_{ijkl}(t)) \right\}, \end{aligned} \quad (10)$$

where  $\theta$  is the spin flip probability per unit time,  $X_{i,j}^{\delta}$ ,  $Y_{ij,kl}^{\delta\delta'}$  and  $W_{ijkl,mnop}$  are the path variables for the flipping from one spin configuration to another designated by the subscript(s) before (at time  $t$ ) and after (at time  $t + \Delta t$ ) the comma sign, on a point, pair and tetrahedron clusters over the specified sublattice(s), respectively, and  $\Delta E$  is the change of the internal energy before and after the flipping events.

In the *PPF*, the first factor  $P_1$  describes the statistical average of non-correlated spin flip events over entire lattice points, and the second factor  $P_2$  is the conventional thermal activation factor. Hence, the product of  $P_1$  and  $P_2$  corresponds to the Boltzmann factor in the free energy and gives the probability that one of the paths specified by a set of path variables occurs. The third factor  $P_3$  characterizes the PPM. One may see the similarity with the configurational entropy term of the CVM (see eq.(5)), which gives the multiplicity, i.e. the number of equivalent states. In a similar sense,  $P_3$  can be viewed as the number of equivalent paths, i.e. the degrees of freedom of the microscopic evolution from one state to another. As was pointed out in the Introduction section, mathematical representation of  $P_3$  depends on the mechanism of elementary kinetics. It is noted that eqs.(8)-(10) are valid only for a spin kinetics.

The *path variables* of the PPM corresponds to the cluster probabilities of the CVM by which the free energy is minimized to obtain the most probable state. Likewise, under a set of constraints, the *PPF* is maximized with respect to the path variables for each time step, which yields the optimized set of path variables. Since a set of path variables,  $\Xi_{\psi,\phi}(t; t + \Delta t)$ , relates cluster probabilities  $\chi_\psi(t)$  at time  $t$  and  $\chi_\phi(t + \Delta t)$  at time  $t + \Delta t$  through

$$\chi_\phi(t + \Delta t) = \chi_\psi(t) + \sum \Xi_{\psi,\phi}(t; t + \Delta t), \quad (11)$$

where  $\psi$  and  $\phi$  represent clusters, one can pursue the time evolution of cluster probabilities  $\chi$  with a given set of initial cluster probabilities.

### 3. High resolution image of atomic configuration

It is recalled that an advantage of the PPM is that not only long range but also short range order kinetics are clarified, which facilitates detailed studies of ordering transitions. However, correlations beyond the specified largest cluster size are not explicitly derived. In fact, it is not theoretically justified to obtain a correlation on a specified cluster from a knowledge of cluster correlations contained in the cluster of interest. This deficiency is, in fact, common to CVM. In order to produce an entire picture of configuration in a given crystal, a subsidiary technique is required. In the present study, Gehlen-Cohen's procedure [27] is employed to synthesize atomic configuration in a model crystal. This technique has been employed to visualize atomic configuration of an entire lattice from the knowledge of finite set of order parameters. Based on the derived cluster concentrations of a point,  $x_i^\alpha$ , and three kinds of pair clusters,  $y_{ij}^{\alpha\alpha}, y_{ij}^{\alpha\beta}, y_{ij}^{\beta\beta}$ , atomic configuration is synthesized in a model fcc crystal which contains  $25 \times 24 \times 21$  lattice points.

The results are demonstrated in Fig. 2 [22, 24, 28] for which the system of 1:1 stoichiometry is quenched from  $T=2.5$  down to 1.7 with an infinite cooling rate and is subject to isothermal aging operation. Each snapshot indicates a resultant atomic configuration on a (100) plane at a time specified by an arrow. Note that the time  $t$  is the normalized with respect to spin flip probability,  $\theta$ , throughout the present study. The left-hand figure corresponds to the equilibrium state at  $T=2.5$  before the quenching operation. Also shown in the figure are the comparison of the input long range (solid line) and short range (broken line) order parameters with the resultant ones (open circle and triangle). It is confirmed that the input information are faithfully realized in the model crystal.

One can see that ordering reaction proceeds abruptly around time  $t = 40,000 \sim 45,000$  leading to the formation of  $L1_0$  ordered phase characterized by a layered arrangement of  $A$  and  $B$  atoms alternatively along the [100] direction as is shown in the uppermost right-hand figure. It was amply discussed in the previous papers that, in the flat portion of



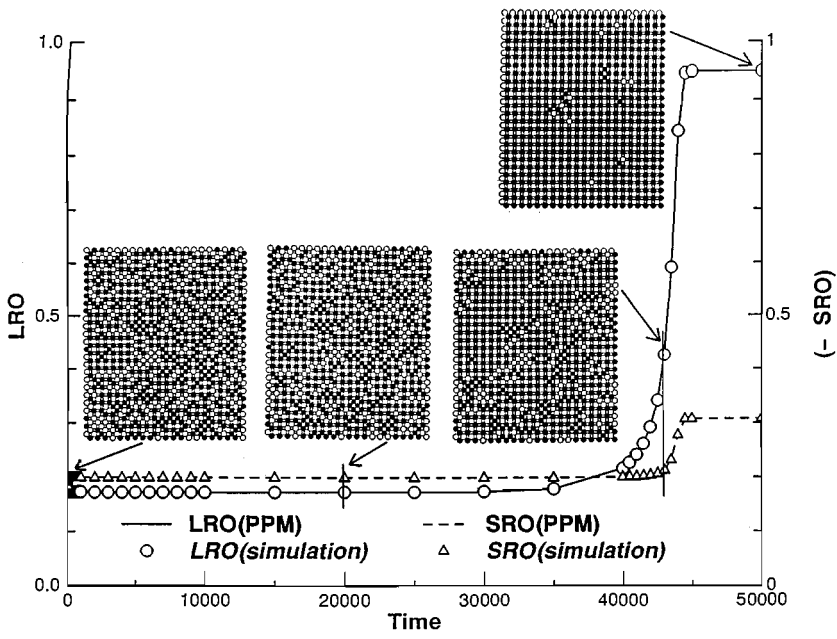


Figure 2: Time sequence of the spin configuration on a (100) plane at 50% when the system at  $T=2.5$  (snapshot a) is quenched down to  $T=1.7$  and is subject to an isothermal aging. Snapshots demonstrated in figs. b, c and d correspond to time  $t=20,000$ ,  $43,000$  and  $50,000$ . The long range and short range order parameters input from the PPM calculations and resultant ones in the simulated lattice are also demonstrated [22, 24, 28] .

the order parameters up to  $t \sim 40,000$ , the system is located closed to the saddle point of the free energy surface, implying the insufficiency of thermodynamic driving force. It should be emphasized again that this portion is not necessarily corresponding to *incubation* period of nucleation events. In fact, the symmetry of entire lattice is already altered to the one for  $L1_0$  ordered phase by the imposition of additional chemical potential at the quenching period. The detailed study of time evolution reveals that the three dominant pair probabilities,  $y_{AA}^{\alpha\alpha}$ ,  $y_{AB}^{\alpha\beta}$  and  $y_{BB}^{\beta\beta}$  change from 0.297 to 0.489, 0.382 to 0.556 and 0.300 to 0.489, respectively, between time  $t=1$  and  $43,000$ . These evolution behavior clearly suggests that the ordering reaction proceeds by adjusting the arrangement via nearest neighbor pair.

Among cluster probabilities derived by the PPM, multibody correlations including triangle and tetrahedron cluster probabilities are not input in the simulation procedure. It is, however, worth noting that the agreements between the calculated multibody correlations and resultant ones in the simulated crystal are fairly reasonable. This is rather encouraging to go further discussions of the visualized configuration.

Shown in Fig. 3 [29] is the high resolution electron micrograph of Cu-Au  $L1_0$  ordered phase at  $400^\circ\text{C}$  taken by Watanabe et al. Black and white dots indicate different atomic species. One may think that the visualized PPM results in Fig. 2 are directly compared with this kind of high resolution image. It should be, however, realized that the comparison of images from a restricted area merely provides qualitative information, since the statistical fluctuation is involved in snapshots obtained both by high resolution experiment and by PPM calculations. Despite this, it is evident that Anti Phase Domain (hereafter APD) contrasted as black stripes in the high resolution micrograph are not observed in the PPM results. Since the area covered in each snapshot in Fig. 2 is nearly one fourth of the

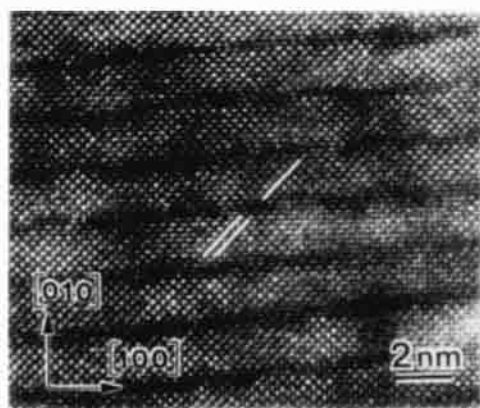


Figure 3: High resolution electron micrograph for Cu-Au  $L1_0$  ordered phase [29] . Black and white dots indicate different species and black stripes are Anti Phase Domain boundaries. The lattice mismatch across the domain boundary is clearly observed by referring to the guide lines in white.

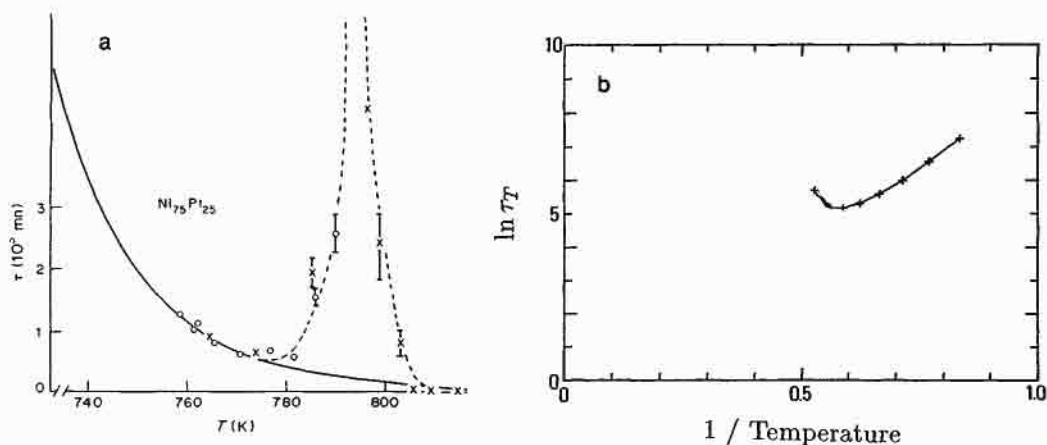


Figure 4: Relaxation time as a function of temperature (or inverse) for a :  $Ni_{75}Pt_{25}$  reported by Dahmani et al. [31] and for b :  $L1_0$  stoichiometry obtained by the PPM calculation [32].

high resolution micrograph, the disappearance of the APD image is not caused by the difference in size but should be ascribed to intrinsic deficiency of the PPM. In fact, the present PPM calculation is limited to homogeneous ordering reaction and heterogeneous ordering reaction characterized by the nucleation-growth of ordered domain is beyond the scope of the conventional PPM. One may artificially introduce nucleation sites in a model crystal, which superficially induces the APD. But more careful study is required for the nucleation event within the framework of the PPM.

#### 4. Electrical resistivity and Ordering Kinetics

The comparison of the images of atomic configuration in the previous section should be regarded as a complementary means to more quantitative ones. Among various experimental techniques, measurement of electrical resistivity is one of the most conventional

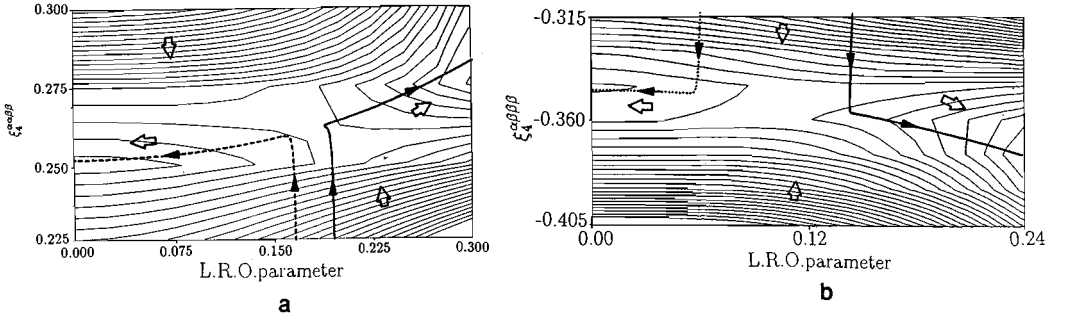


Figure 5: Free energy surface at 1:1 (Fig. 5a) [22, 24, 28] and 1:3 (Fig. 5b) [23, 24, 33] stoichiometries in the vicinity of disordered state ( $\xi_4^\alpha = 0.0$ ) at  $T = 1.70$  and  $1.6$ , respectively. The solid line in left-hand (right-hand) figure indicates the kinetic path evolving towards the  $L1_0$  ( $L1_2$ ) ordered phase when the system is quenched from  $T = 2.5$  ( $3.0$ ) down to  $1.70$  ( $1.60$ ), while the broken lines are devolving towards disordered phase. The open arrows on the contour surface designate the direction of the decrease of free energy, and the arrows on the kinetic path indicate the direction of time evolution or devolution.

methods for a quantitative discussion. In order to compare the absolute value of electrical resistivity, it is indispensable to refer to the electronic structure of an alloy system, in particular, the Density Of States. This is, however, beyond the scope of the present study and we confine ourselves only to the relative change with respect to a suitable reference state.

By employing Rossiter's formula [30] given by

$$\frac{\rho_0(\eta)}{\rho_0(0)} = \frac{1 - \eta^2}{1 - A\eta^2}, \quad (12)$$

where  $A$  is a materials constant and  $\eta$  is the long range order parameter, derived cluster probabilities are converted into the relative electrical resistivity  $\rho_0(\eta)/\rho_0(0)$  where  $\rho_0(\eta)$  and  $\rho_0(0)$  are electrical resistivities for an alloy at a certain state of order specified by  $\eta$  and some reference state, respectively. Note that the long range order parameter  $\eta$  is defined, in the present study, as the difference of the point cluster probabilities between the two sublattices,  $x_i^\alpha - x_i^\beta$ .

Shown in Fig. 4a is the temperature dependence of the relaxation time obtained from the isothermal electrical resistivity measurement for  $Ni_3Pt$  performed by Dahmani et al [31]. A prominent feature is the appearance of *slowing down* phenomenon near transition temperature. As is shown in Fig. 4b [32], our PPM calculation is able to reproduce similar phenomenon, although the present study is attempted to  $L1_0$  ordered phase for which the transition temperature,  $T_c$ , is  $\sim 1.89$ . One can confirm that the relaxation time,  $\tau$ , increases as approaching to  $1/T_c \sim 0.52$ . This has been explained as the insufficiency of the thermodynamic driving force near the transition temperature in the following manner.

Alternative to the cluster probabilities,  $x_i^\delta, y_{ij}^{\delta\delta'}, z_{ijk}^{\delta\delta'\delta''}, w_{ijkl}^{\delta\delta'\delta''\delta'''}$ , in describing atomic configuration are the set of atomic correlation functions  $\{\xi\}$  defined as an ensemble average of spin operator [34, 35, 36]. Various advantages of the employment of the correlation functions stem from the fact that the correlation functions form an independent set of configurational variables. In terms of correlation functions, the free energy functional for  $L1_0$  and  $L1_2$  ordered phases are formally expressed as

$$F^{L1_0} = F(T, \xi_1^\alpha, \xi_1^\beta, \xi_2^\alpha, \xi_2^\beta, \xi_2^\beta, \xi_3^\alpha, \xi_3^\beta, \xi_4^\alpha, \xi_4^\beta) \quad (13)$$

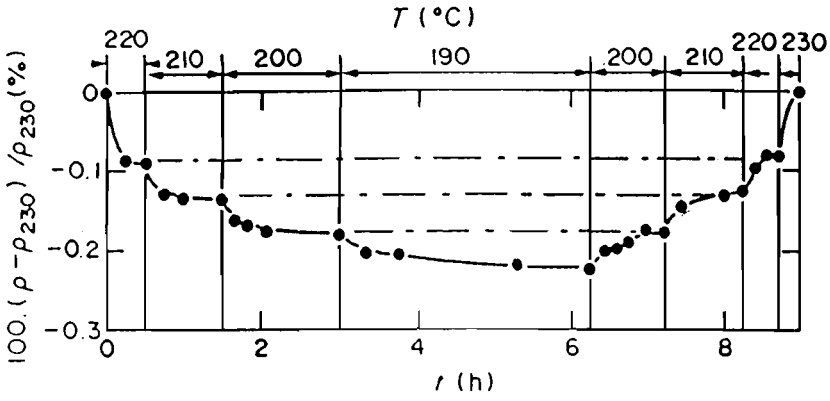


Figure 6: Relative change of electrical resistivity measured for Ag-3.5at%Al system at isothermal aging period with falling and rising temperatures [38] .

and

$$F^{L_{12}} = F(T, \xi_1^\alpha, \xi_1^\beta, \xi_2^{\alpha\beta}, \xi_2^{\beta\beta}, \xi_3^{\alpha\beta\beta}, \xi_3^{\beta\beta\beta}, \xi_4^{\alpha\beta\beta\beta}), \quad (14)$$

respectively, where subscript and superscript indicate a size of the cluster and a sublattice point(s) in which the cluster is located. Then, the minimization of free energy functional under a constraint of specified temperature  $T$  and a set of correlation functions,  $\{\xi^*, \xi^{**}\}$ , provides free energy contour surface spanned in the two dimensional space with  $\xi^*$  and  $\xi^{**}$  as orthogonal axes. Figures 5a [22, 24, 28] and 5b [23, 24, 3] are the magnified portions of the contour surface near disordered state calculated for  $L_{10}$  stoichiometry at  $T=1.70$  and for  $L_{12}$  stoichiometry at  $T=1.60$ , respectively, by choosing point correlation function,  $\xi_1^\alpha$ , and tetrahedron correlation function,  $\xi_4$ , as  $\xi^*$  and  $\xi^{**}$ . It is noted that the point correlation function,  $\xi_1^\alpha$ , itself is the long range order parameter and that the tetrahedron correlation function,  $\xi_4$ , serves as a short range order parameter. In Fig. 5a, one can readily see that the gradient of the free energy contour surface is rather flat in the direction of the long range order parameter ( $\xi_1^\alpha$ ) forming a saddle point. The flatness is further pronounced as approaching transition temperature, which implies the lack of thermodynamic driving force, leading to a longer relaxation time as demonstrated in Fig. 4b. As is shown in Fig. 5b, the similar morphology of the free energy configuration is observed for  $L_{12}$  stoichiometry. We believe this is responsible for the observed *slowing down* phenomenon in Fig. 4a.

Pfeiler and his coworkers performed a series of measurements on various alloy systems such as Cu-Au, Ag-Al, Ni-Al etc [37]. Among them, a typical experiment constitutes isothermal anneals at falling and rising temperatures after equilibrium state at each temperature is attained. Shown in Fig. 6 is a representative result obtained for Ag-3.5at%Al [38]. The vertical axis is the relative change of electrical resistivity while the horizontal axis is the time or, equivalently, the temperature. One can confirm that the time elapsed until equilibrium is attained is prolonged with decreasing temperature. By examining the reproducibility of the overall curve, the validity of the PPM is further discussed in the following.

The calculated results are demonstrated in Figs. 7a and 7b [25, 33]. The system maintained at  $T=1.85$  is subject to down quenching with a temperature step  $\Delta T = 0.05$  and isothermal aging is followed at each temperature to equilibrate the system. After reaching the equilibrium at  $T=1.5$ , the operation is reversed up to  $T=1.85$ . In Fig. 7a, one sees that the resultant relaxation time is shortened with decreasing temperature and

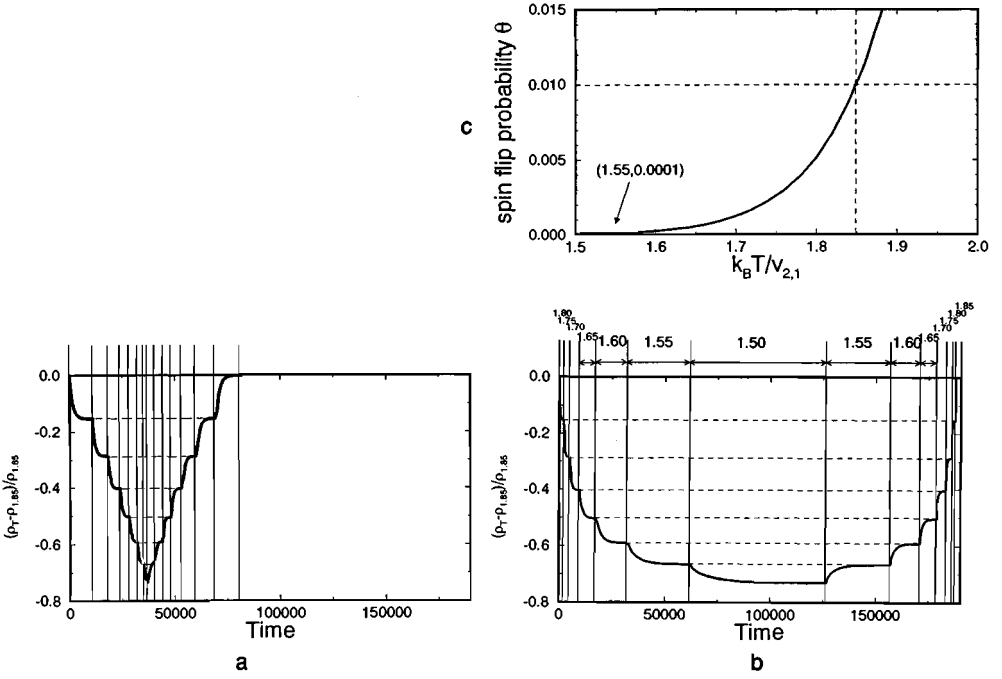


Figure 7: Relative change of electrical resistivity during isothermal aging condition with falling and rising temperatures obtained by PPM calculations [25, 33] without (a) and with (b) incorporating thermal activation process in the spin flip probability  $\theta$ . The assumed temperature dependency of  $\theta$  is indicated in figure c.

the entire curve is unacceptably distorted as compared with the experimental one in Fig. 6. This inconvenience is explained as follows.

According to eq.(12) the resistivity change is caused by the contribution of atomic configuration characterized by the long range order parameter,  $\eta$ . For the *disorder-L1<sub>2</sub>* transition which is a typical first order transition, a drastic change of a long range order parameter takes place near the transition temperature, which is reflected as the pronounced change of relative resistivity in the higher temperature region in Fig. 6. This, however, implies that if merely the change of state of order is responsible for the resistivity, the resultant relaxation time is necessarily to be pronounced in the higher temperature region as is shown in Fig. 7a, which is far from reality.

It is recalled that the elementary atomic migration by breaking bondings with surrounding atoms is also driven by thermal activation process. This is modeled through the incorporation of the activation barrier,  $\Delta G^*$ , in the spin flipping event via the following equation,

$$\theta = \nu \exp \left( -\frac{\Delta G^*}{k_B T} \right), \quad (15)$$

where  $\nu$  is the attempt frequency. As is shown in Fig. 7b for which  $\Delta G^*$  is assigned so that the resultant spin flip probability at  $T=1.85$  is one hundred times bigger than that at  $T=1.55$  (see Fig. 7c), the introduction of the temperature dependency into  $\theta$  satisfactorily reproduces the overall feature of experimental curve. We note that this dependency is certainly incorporated in the calculation in Fig. 4b.

A detailed study conducted by Kozubski et al. [39], however, revealed that the relaxation process is not described by a single mechanism. Their result clearly suggests that the

relaxation curve composed of two independent processes, quick process in the initial period and a rather slow one in the latter stage. We believe that affluent feature of diffusion process result in the multi-fold relaxation processes. This may not be easily reproduced by the present PPM calculation for a spin system. It is clear that the further progress with PPM calculation for fcc-based system demands the incorporation of the vacancy mechanism. We believe this is the most important direction of the future investigation of the PPM.

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# THE MARTENSITIC TRANSFORMATION IN IRON-NICKEL ALLOYS: A MOLECULAR DYNAMICS STUDY

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## INTRODUCTION

Many metals and metallic alloys show martensitic transformations at temperatures below the melting point. Martensitic transformations are structural phase changes of first order which belong to the broader class of diffusionless solid-state phase transformations. These are structural transformations of the crystal lattice, which do not involve long-range atomic movements. A recent review of the properties and the classification of diffusionless transformations has been given by Delaey<sup>1</sup>.

Though martensitic transformations have been studied for a long time, there are many open questions. The phenomenological crystallographic theory as described by Wayman<sup>2</sup> or Haasen<sup>3</sup> describes the martensitic transformation on a microscopic scale in terms of a lattice deformation, a rotation and an inhomogeneous shear. But so far there is only little known about the atomic processes leading to the transformation. Especially the nucleation of the formation of the low-temperature structure (martensite) into the high-temperature parent lattice (austenite) is subject of rather controversial discussions. Another outstanding problem is the influence of vacancies and other defects on the transformation.

Martensitic transformations occur as well in magnetic as in non-magnetic systems. But there are considerable differences between these two cases. The non-magnetic alloys showing a martensitic transformation, normally crystallize at the melting point in a bcc structure which transforms during the martensitic transformation into a close-packed structure. On heating the reverse transformation occurs with only a small hysteresis. On the other hand the magnetic systems (normally ferrous alloys) showing a martensitic transformation, crystallize in a fcc structure which is transformed into a bcc martensite. The reverse transformation thereby shows huge temperature hysteresises of 100 K and more.

The rest of this paper will be organized as follows: In the next section we describe a set of interatomic potentials which we have developed to model iron-nickel alloys and report the calculational techniques of molecular dynamics simulations which we



have done in order to study the martensitic transformation in  $\text{Fe}_x\text{Ni}_{1-x}$  alloys. Then we present results which we have obtained from these simulations. We have especially looked for the orientational relationships between the austenitic and the martensitic lattice and the formation of an inhomogeneous shear during the transformation in our calculations. We also have studied the influence of point defects on the transformation. The last section is devoted to a short discussion of our results.

## COMPUTATIONAL DETAILS

### Interatomic Potentials

We have used the embedded-atom method (EAM) <sup>4, 5</sup> to develop interatomic potentials suitable for the simulation of iron-nickel alloys. In this method the total energy of the alloys can be written as

$$E = \sum_i \mathcal{F}_i(\rho_i) + \sum_{i \neq j} \frac{Z_i(r_{ij}) Z_j(r_{ij})}{r_{ij}}, \quad (1)$$

where  $r_{ij}$  is the distance between the atoms  $i$  and  $j$  and

$$\rho_i = \sum_{j \neq i} \rho_j^{at}(r_{ij}) \quad (2)$$

is an effective electronic density at the position of atom  $i$ .  $\rho_i$  is the sum of individual contributions  $\rho_j^{at} = \rho_{\text{Fe}}^{at}$ , or  $\rho_{\text{Ni}}^{at}$  of all the atoms  $j$  surrounding atom  $i$ . The first term in (1) is the embedding energy of the system with the embedding functions  $\mathcal{F}_i = \mathcal{F}_{\text{Fe}}$ , or  $\mathcal{F}_{\text{Ni}}$ . The second part is a pair potential which is assumed to be of Coulomb form, where  $Z_i = Z_{\text{Fe}}$ , or  $Z_{\text{Ni}}$  represent screened ionic charges.

Like Daw and Baskes<sup>5</sup>, we use the double-zeta wave functions  $\Phi$  of Clementi and Roetti<sup>6</sup> for the calculation of the effective electronic densities

$$\rho_i^{at}(r) = n_{4s} \Phi_{4s}^2(r) + (N_{val} - n_{4s}) \Phi_{3d}^2(r). \quad (3)$$

These functions are truncated and shifted to zero at a cutoff-distance  $r_c$  between the third and fourth nearest neighbor shell.  $N_{val}$  is the number of valence electrons and  $n_{4s}$  is a parameter. Following Daw and Baskes further on we use cubic spline functions to represent the functions  $\mathcal{F}_i(\rho)$  and  $Z(r)$ . The splines have been fitted to the experimental values of lattice constant, cohesive energy, vacancy formation energy, elastic constants and some high symmetry phonon frequencies of pure Ni and Fe. The results are given in Tab 1. The values of  $n_{4s}$  have only little influence on the properties of the potentials for the pure metals. Therefore, these values have been chosen by hand to give an overall good description of the alloy properties.

Results concerning thermodynamic properties which we have obtained from molecular dynamics simulation with these potentials and the transition temperatures of the martensite – austenite transition we found, have been published elsewhere<sup>7</sup>.

### Molecular Dynamics Simulations

In our calculations we make use of several standard techniques of molecular dynamics simulations<sup>8</sup>. The integration of the equations of motions is done by the velocity form of the Verlet-algorithm<sup>9</sup> with a time step of  $1.5 \cdot 10^{-15} \text{ s}$ . The temperature is controlled by a Nosé-thermostat<sup>10, 11</sup> and the method of Parrinello and Rahman<sup>12, 13</sup> is adopted in

**Table 1.** Parameters of the interatomic potentials. Distances are given in  $a_B$ , densities in  $a_B^{-3}$ , charges in  $e^-$  and energies in Ry.  $n_{4s}$  and  $r_c$  have been set to 0.57 and 8.33  $a_B$  for iron. The corresponding values for nickel are 0.85 and 8.78  $a_B$ ;  $a_0$  denotes the equilibrium lattice constant of the elements;  $\rho_0$  is the electron density at equilibrium for the perfect lattices, i.e. 0.002776  $a_B^{-3}$  and 0.003543  $a_B^{-3}$  for iron and nickel respectively.

| $r$          | $Z_{Fe}(r)$              | $Z'_{Fe}(r)$               | $r$          | $Z_{Ni}(r)$              | $Z'_{Ni}(r)$               |
|--------------|--------------------------|----------------------------|--------------|--------------------------|----------------------------|
| 0.0          | 26.0                     | 0.0                        | 0.0          | 28.0                     | 0.0                        |
| 0.70 $a_0$   | 1.4403                   |                            | 0.60 $a_0$   | 0.9874                   |                            |
| 0.87 $a_0$   | 0.2452                   |                            | 0.71 $a_0$   | 0.1596                   |                            |
| 0.94 $a_0$   | 0.1491                   |                            | 0.85 $a_0$   | 0.0                      | 0.0                        |
| 1.00 $a_0$   | 0.0734                   |                            |              |                          |                            |
| 1.20 $a_0$   | 0.0                      | 0.0                        |              |                          |                            |
| $\rho$       | $\mathcal{F}_{Fe}(\rho)$ | $\mathcal{F}''_{Fe}(\rho)$ | $\rho$       | $\mathcal{F}_{Ni}(\rho)$ | $\mathcal{F}''_{Ni}(\rho)$ |
| 0.0          | 0.0                      | 0.0                        | 0.0          | 0.0                      | 0.0                        |
| 0.5 $\rho_0$ | -0.2823                  |                            | 0.5 $\rho_0$ | -0.2695                  |                            |
| 1.0 $\rho_0$ | -0.4276                  |                            | 1.0 $\rho_0$ | -0.3961                  |                            |
| 2.0 $\rho_0$ | -0.3030                  |                            | 2.0 $\rho_0$ | -0.2654                  |                            |
| 2.3 $\rho_0$ | 0.0                      | 0.0                        | 2.3 $\rho_0$ | 0.0                      | 0.0                        |

order to enable changes of the simulation box. Periodic boundary conditions apply for all directions.

We have done simulations starting with five different initial configurations, which are described in Table 2. All systems were equilibrated over 1000 MD steps at 300 K. Then for the systems A - D the temperature was gradually increased, doing 5000 MD steps at each temperature and another 250 equilibration steps at each new temperature, until the martensite - austenite transition occurred. Afterwards the temperature of systems A, C and D was decreased until the system again showed a bcc structure. The treatment of system E was slightly different. This configuration was first cooled until the martensite structure occurred. Then it was heated and cooled again like the other systems.

**Table 2.** Parameters of the starting configurations for the simulations. The lattices were aligned with the (100) planes parallel to the sides of the simulation box.

| system | lattice | elementary cells | number of atoms | % iron atoms | % vacancies |
|--------|---------|------------------|-----------------|--------------|-------------|
| A      | BCC     | 17 <sup>3</sup>  | 9826            | 80           | 0           |
| B      | BCC     | 17 <sup>3</sup>  | 9826            | 65           | 0           |
| C      | BCC     | 12 <sup>3</sup>  | 3378            | 80           | 2           |
| D      | BCC     | 16 <sup>3</sup>  | 8019            | 80           | 2           |
| E      | FCC     | 13 <sup>3</sup>  | 8192            | 80           | 0           |

## RESULTS

The martensite - austenite transition temperatures we find are for all systems in accordance with the previously published ones<sup>7</sup>. Some minor deviations can be attributed to the fact that we are simulating an overheated first order phase transition. Therefore, for our limited system sizes, one cannot expect a definite transition temperature.

In contrast to this the austenite – martensite transition temperature depends on the concentration of vacancies. The configurations A and E show a transition temperature of 10 K, while in C and D the bcc structure already occurs at 100 K.

We found that without any exception in all of our simulations Bain's lattice correspondence actually applies, i.e. one set of (110) planes of the bcc structure corresponds to a set of fcc (111) planes, while the bcc [001] direction lying in these planes is transformed into the  $[\bar{1}\bar{1}0]$  direction of the fcc phase. Moreover, these directions are exactly parallel to each other. This would correspond to a Nishiyama-Wassermann orientational relationship<sup>1, 14</sup>, if the (110) and (111) planes would also be parallel to each other. But this is not the case. These planes are rotated around [001] by an angle between  $0^\circ$  and  $9^\circ$  during the transformation. This angle differs between the simulations in a non-systematic way.

Fig. 1 shows the austenite structure which has formed in configuration A along the (unrotated)  $[\bar{1}\bar{1}0]_{\text{fcc}}$  direction. One can see the top two layers of atoms. The fcc phase in this system has formed rather regularly, with 6 stacking faults, which can easily be seen at the borders of Fig. 1. These stacking faults lead to a shear of the crystal, which reduces the atomic movement during the transformation. The same stacking faults evolved during the martensite – austenite transition in configurations B and E. Fig. 2 similarly shows the austenite structure of system D. Small agglomerates of atoms (not necessarily confined to the two top layers of atoms) which can be seen in this figure are due to the structural disorder caused by vacancies situated beneath these agglomerates. It is also obvious from this figure that the vacancies lead to a big number of stacking faults in the austenitic phase which no longer has fcc structure but an irregular closed packed structure.

After a full transformation cycle, i.e. one austenite – martensite and one martensite – austenite transition, we find a striking difference between the perfect configurations and those with vacancies: Only the systems with defects regain the initial cubic form of the simulation box.

## DISCUSSION

The transition temperatures which we find for the austenite – martensite transition in simulations without vacancies, are much too low. The introduction of vacancies lead to much more physical results, while the martensite – austenite transition is not affected by vacancies. From this we conclude that vacancies lower the energy barrier which the system has to overcome during the transition. The reason for this might be a weakening of long-range elastic couplings in the lattice.

The orientational relationships between the martensite and austenite lattice which we observe are partially in accordance with experimental results: In experiments a Nishiyama-Wassermann relationship is found for those systems which we have simulated. We think that the additional rotation of the  $(111)_{\text{fcc}}$  planes in the simulations is an effect of boundary conditions. Experimentally bcc and fcc structure coexist and the plane of contact, the habit plane, is undistorted. In our simulations we have no coexistence of these structures. But the periodic boundary conditions play a similar role like the habit plane in the real crystals. Under these considerations the fact that we find the same invariant direction as it is observed experimentally shows, that our calculations simulate the same transition process as it takes place in experiments. The same is true for the inhomogeneous shear system which we see in our simulations.

From the fact that only systems with vacancies regain the form of the simulation box

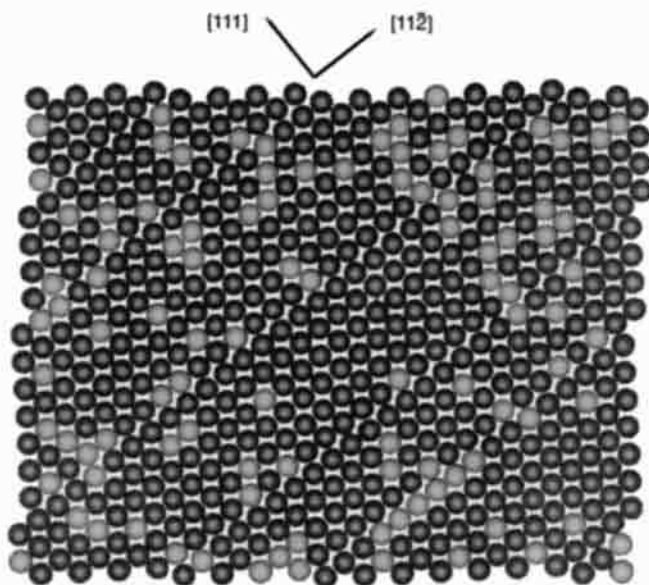


**Figure 1.** Austenite phase of configuration A viewed along the  $[1\bar{1}0]$  direction. Dark spheres represent iron atoms, bright spheres nickel atoms.

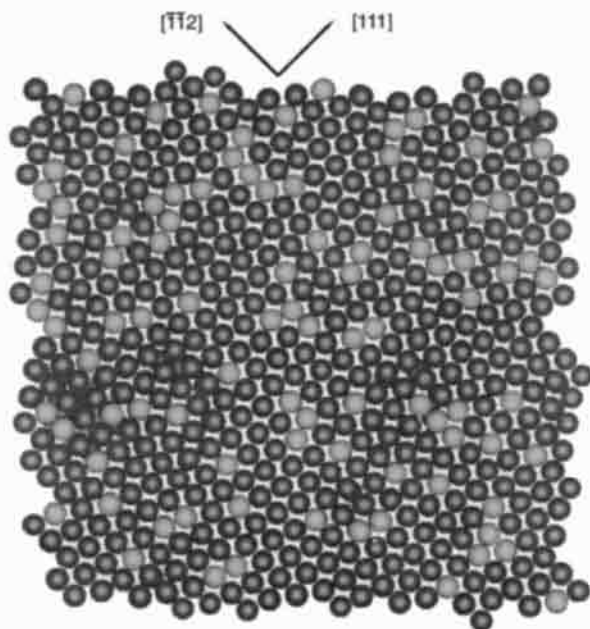


**Figure 2.** Austenite phase of configuration D viewed along the  $[1\bar{1}0]$  direction. Dark spheres represent iron atoms, bright spheres nickel atoms.

after a full transformation cycle, it is obvious that in our model system the vacancies induce a shape memory effect in the sense that there is a preferred transformation direction which controls the formation of a special variant.

At the moment it is not clear how far our first results concerning the role of defects are influenced by the vacancy concentration of 2%. We have used this rather high concentration in order to have a significant number of vacancies in our systems. It will be necessary to make further simulations using more moderate vacancy concentrations and probably other kinds of defects to get a real understanding of the role of defects in martensitic transformations.

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## KINETICS AT EARLY STAGES OF PHASE TRANSFORMATIONS IN METALLIC ALLOYS

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### 1. Introduction

Problems of the theoretical description of nonequilibrium statistical systems are important for various areas of physics. For equilibrium systems, such a description is given by the Gibbs distribution and statistical thermodynamics, but for states far from equilibrium there are no analogous standard approaches available. The elaboration of suitable approaches is of particular interest for configurational alloy kinetics, the evolution of the atomic distribution in nonequilibrium alloys. The microstructure and macroscopic properties of such alloys, e.g. strength and plasticity, depend crucially on their thermal and mechanical history, for example, on the particular kinetic path of the phase transformation. A number of theoretical approaches have been proposed in that field, e.g.<sup>1-3</sup>. However, these approaches either treat the uniform alloy case<sup>1</sup> which excludes from consideration most applications of interest, or use various unclear approximations, such as the extrapolation of the linear Onsager equation for weakly nonequilibrium states to the nonlinear region of states far from equilibrium<sup>2,3</sup>, which can result in significant errors<sup>4,5</sup>.

Recently<sup>4-6</sup> we proposed to describe the nonequilibrium alloy kinetics using the fundamental master equation for probability  $P$  of finding the occupation number set  $\{n_i\} = \alpha$ , for example, in a binary alloy A-B, where  $n_i = n_i^A = 1$  if the site  $i$  is occupied by an A atom, and  $n_i = 0$  otherwise:

$$dP(\alpha)/dt = \sum_{\beta} [W(\alpha, \beta)P(\beta) - W(\beta, \alpha)P(\alpha)] \quad (1)$$

Here  $W(\alpha, \beta)$  is the  $\beta \rightarrow \alpha$  transition probability for which we accept the conventional "thermally activated atomic exchange model"<sup>1,7,8</sup>. Below we briefly review several recent works on the general formulation of this approach and on its applications to studies of alloy phase transformations.

## 2. Master equation approach: exact relations and cluster approximations<sup>9</sup>

The general expression for  $P\{n_i\}$  in Eq. (1) for a binary alloy can be written as

$$P\{n_i\} = \exp[\beta(\Omega + \sum_i \lambda_i n_i - Q)] \quad (2)$$

Here  $\beta = 1/T$ , the correlative term  $Q$  is an analogue of the hamiltonian  $H$ :

$$Q = \sum_{i>j} a_{ij} n_i n_j + \sum_{i>j>k} a_{ijk} n_i n_j n_k + \dots \quad (3)$$

$$H = \sum_{i>j} v_{ij} n_i n_j + \sum_{i>j>k} v_{ijk} n_i n_j n_k + \dots, \quad (4)$$

while  $\lambda_i$  and  $a_{i\dots j}$  are the distribution parameters. The "generalised grand canonical potential"  $\Omega = \Omega\{\lambda_i, a_{i\dots j}\}$  is determined by the normalization condition:

$$\Omega = -\ln \text{Tr} \exp(\sum_i \lambda_i n_i - Q) \quad (5)$$

where  $\text{Tr}(\dots) = \sum_{\{n_i\}}(\dots)$  means summation over all configurations.

Multiplying the master equation by operators  $n_i, n_i n_j$ , etc. and summing the results over all configurations, we obtain the exact system of equations for the mean occupations  $c_i(t) = \langle n_i \rangle$  and correlators  $g_{i\dots j}(t) = \langle n_i \dots n_j \rangle$ , where  $\langle \dots \rangle = \text{Tr}(\dots)P$  stands for the average over the distribution  $P$ . These equations enable us to derive the microscopic expression for the free energy  $F$  of the nonequilibrium state. The function  $F\{c_i, g_{i\dots j}\}$  has a fundamental property not to increase under spontaneous evolution, similarly to the Boltzmann non-decreasing entropy:

$$F = \Omega + \sum_i \lambda_i c_i + \langle H - Q \rangle \quad (6)$$

$$dF = \sum_i \lambda_i dc_i + \sum_{i>\dots>j} (v_{i\dots j} - a_{i\dots j}) dg_{i\dots j} \quad (7)$$

$$dF/dt \leq 0 \quad (8)$$

The stationary state (being not necessarily uniform) corresponds to the minimum of  $F$  at given  $N = \sum_i c_i$ :

$$\frac{\partial}{\partial c_i}(F - \mu N) = 0, \quad \frac{\partial F}{\partial g_{i\dots j}} = 0 \quad (9)$$

where  $\mu$  is the Lagrange parameter. Eqs. (7) and (9) yield Gibbs relations for parameters  $\lambda_i$  and  $a_{i\dots j}$  in the stationary distribution  $P\{n_i\}$ :

$$\lambda_i = \mu; \quad a_{i\dots j} = v_{i\dots j} \quad (10)$$

In order to find approximate solutions of the equations for  $c_i(t)$  and  $g_{i\dots j}(t)$  one can use regular approximate methods of statistical physics, such as the mean-field approximation (MFA) and the cluster variation method (CVM), as well as its simplified version, the cluster field method (CFM)<sup>10</sup>. In both MFA and CFM, the equations for  $c_i(t)$  are separated from those for  $g_{i\dots j}(t)$  and take the form

$$\frac{dc_i}{dt} = 2 \sum_s M_{is} \sinh \left[ \frac{1}{2} \beta \left( \frac{\partial F}{\partial c_s} - \frac{\partial F}{\partial c_i} \right) \right] \quad (11)$$

where  $M_{is} = M_{is}\{c_l\}$  and  $F = F\{c_i\}$  are the MFA or CFM expressions for the generalised mobility and the free energy of the nonuniform alloy. For simplest approximations, such as MFA or the pair-cluster approximation (PCA), these expressions can be written out analytically. For example, the MFA expressions for  $M_{is}$  and  $F\{c_i\}$  in the binary alloy are

$$M_{is} = \gamma_{is}(c_i c'_i c_s c'_s)^{1/2} \exp[\beta \sum_l (u_{il} + u_{sl}) c_l / 2] \quad (12)$$

$$F_{\text{MFA}}\{c_i\} = T \sum_i (c_i \ln c_i + c'_i \ln c'_i) + \sum_{i>j} v_{ij} c_i c_j \quad (13)$$

Here  $c'_i = 1 - c_i$ ;  $\gamma_{is}$  is the  $c_i$ -independent factor in the intersite atomic jump probability;  $u_{il} = V_{il}^{\text{AA}} - V_{il}^{\text{BB}}$ , and  $v_{il} = V_{il}^{\text{AA}} + V_{il}^{\text{BB}} - 2V_{il}^{\text{AB}}$ . Substituting Eqs. (13) into (14) we obtain the analytical mean-field kinetic equation (MFKE) for  $c_i(t)$  used in works<sup>4-6</sup>. Similar analytical equation is obtained in PCA. In higher approximations of CFM, such as the "tetrahedron", "octahedron", etc, values of  $M_{is}$  and  $\partial F/\partial c_i$  in Eqs. (11) should be found numerically by solving the algebraic equations of the power 4, 6, etc.

### 3. Kinetic features of phase separation under alloy ordering<sup>5</sup>

Kinetics of phase separation with ordering has been phenomenologically discussed by Allen and Cahn<sup>11</sup> (AC) in their study of Fe-Al alloys, the phase diagram of which is similar to that presented in Fig. 1 in a certain range of concentrations  $c$  and temperatures  $T$ . A number of peculiarities in the microstructural evolution for such phase transformations have been noted, including the possible strong effect of the presence of antiphase boundaries (APB) on the evolution type<sup>11</sup>. Some of the conclusions of AC have been illustrated by computer simulations based on a simplified kinetic equation<sup>3</sup>. Recently we applied MFKE to treat the problem microscopically<sup>5</sup>. Our results illustrate and specify the general considerations of AC and also reveal a number of new effects.

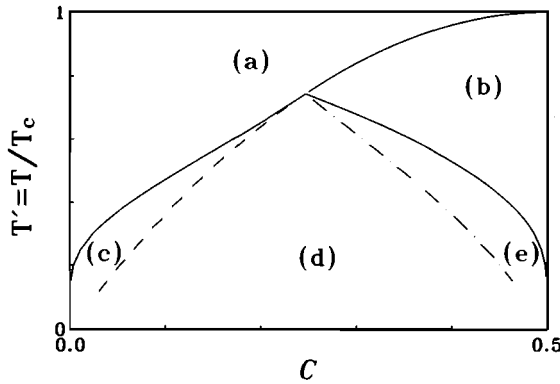


Fig. 1. Equilibrium phase diagram  $(T', c) = (T/T_c, c)$  for the alloy model used in Ref.<sup>5</sup>. Solid lines: boundaries of the disordered (a) and homogeneously ordered (b) fields; areas c, d and e correspond to the two-phase region. Dashed line is the ordering spinodal separating the metastable disordered area c from the spinodal decomposition area d. Dot-dashed line is the conditional spinodal<sup>11</sup> that separates the area d from the ordered metastable area e.



Some evolution types observed in our simulations are shown in Figs. 2-7. The simulations were performed for the same 2D alloy model as that used in Refs.<sup>2,3</sup>, on a square lattice of  $128 \times 128$  sites with periodic boundary conditions. The as-quenched distribution  $c_i(0)$  was characterized by its mean value  $c$  and small random fluctuations  $\delta c_i = \pm 0.01$ . The intersite atomic jumps were supposed to occur only between nearest neighbors:  $\gamma_{ij} = \gamma_{nn}$ , and we used the "reduced" time variable  $t' = t\gamma_{nn}$ .

Fig. 2 illustrates the ordering process after a quench of a disordered alloy below the ordering spinodal. As it was mentioned by AC, the primary ordered domains are formed after few atomic exchanges:  $\Delta t' \lesssim 1$ , while further evolution corresponds to the growth of these domains. Fig. 3 shows that in the absence of APBs the microstructure evolution under spinodal decomposition with ordering is similar to that for disordered

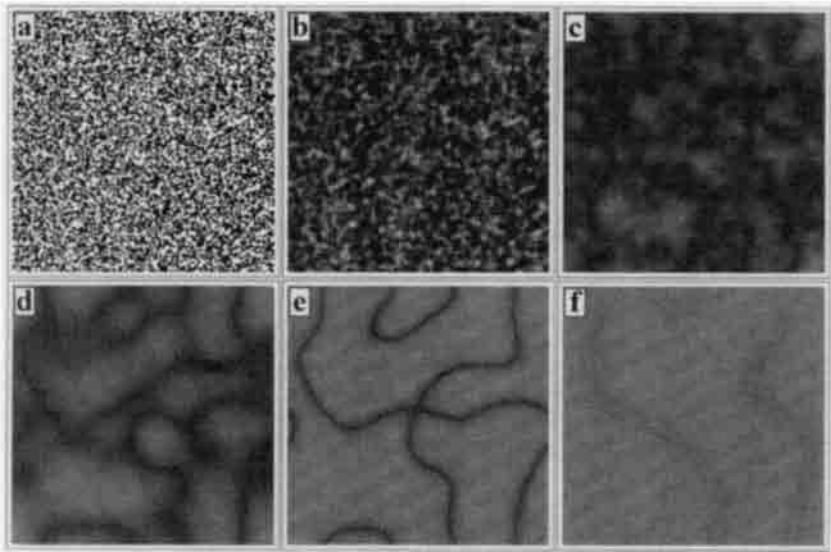


Fig. 2. Temporal evolution of mean occupations  $c_i = c(\mathbf{r}_i)$  for the  $a \rightarrow b$  type quench in Fig. 1, at  $T' = 0.74$ ,  $c = 0.3$ , and following values of  $t' = t\gamma_{nn}$ : (a) 0, (b) 0.5, (c) 2, (d) 5, (e) 10, and (f) 200. The grey level linearly varies with  $c_i$  between its minimum and maximum value for each of Figures 2a-2f; the same coloring is used below in Figs. 8, 10 and 12.

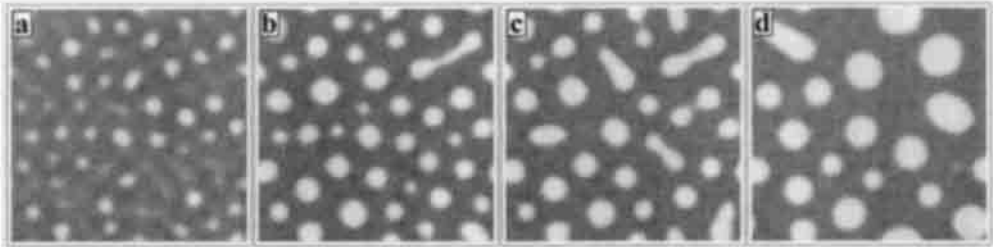


Fig. 3. Temporal evolution of  $c_i$  under spinodal decomposition of a single domain ordered state, at  $T' = 0.42$ ,  $c = 0.325$ , and following  $t'$ : (a) 500, (b) 2000, (c) 3000, and (d) 10000. The grey level in Figs. 3-5 linearly varies with  $c_i$  between  $c_i = 0$  and  $c_i = 1$ .

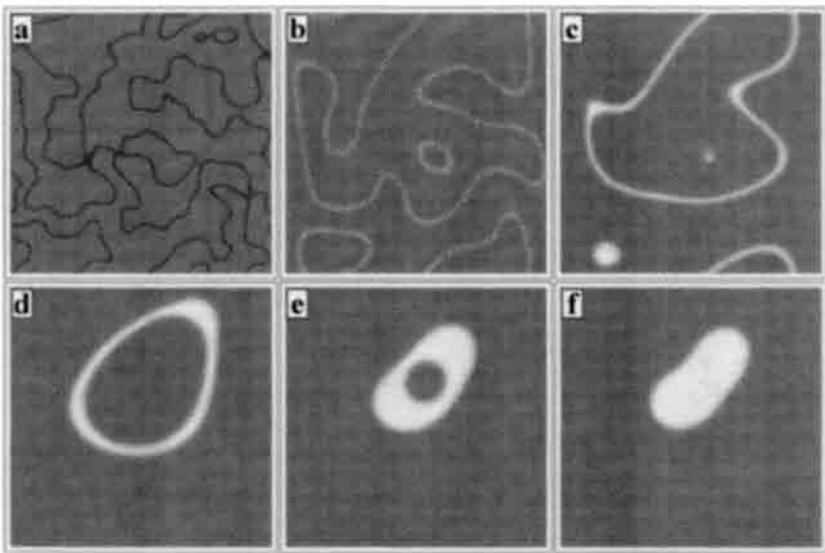


Fig. 4. Temporal evolution of  $c_i$  for the  $a \rightarrow \epsilon$  type quench in Fig. 1, at  $T' = 0.42$ ,  $c = 0.415$ , and following  $t'$ : (a) 1, (b) 10, (c) 1000, (d) 9000, (e) 23000, and (f) 25000.

alloys. In particular, the "coagulation" stage when coarsening is dominated by fusion of precipitates via the "bridge" mechanism<sup>4</sup> is distinctly seen. Fig. 4 shows that after a quench into the metastable ordered state PBs can become embryos for nucleation of the disordered phase<sup>11</sup>; the latter is due to the suppression of the order parameter and the depletion the minority component near APB<sup>6</sup>.

Fig. 5 illustrates a peculiar kinetic phenomenon which occurs when an initially disordered alloy is first annealed at temperature  $T_a$  corresponding to area  $b$  in Fig. 1 and then quenched to the final temperature  $T$  into the spinodal instability area  $d$ : antiphase boundaries "replicate", generating approximately periodic patterns. This phenomenon reflects the presence of critical, fastest growing concentration waves under the spinodal instability (the Cahn waves<sup>12</sup>). Lowering of the temperature to  $T < T_a$  results in lowering of the minority concentration minimum ("c-well") within APB, while the expelled solute atoms build the "c-bank" adjacent to the well<sup>6</sup>. Due to the

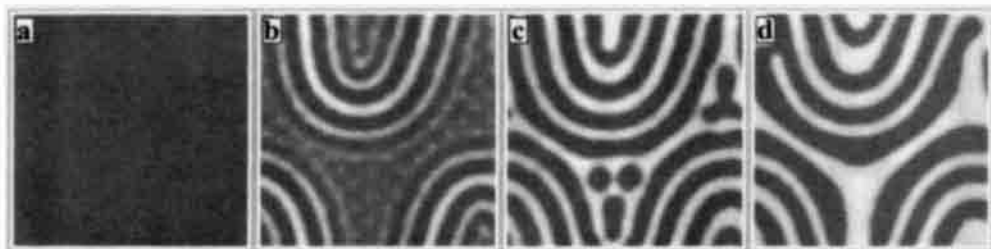


Fig. 5. Temporal evolution of  $c_i$  after the disordered state with  $c = 0.26$  was annealed for  $t'_a = 100$  at  $T'_a = 0.75$ , and then quenched to  $T' = 0.42$ , at following times  $t'$  after the quench: (a) 0 (as-quenched), (b) 200, (c) 1000, and (d) 3000.

spinodal instability this bank does not relax but rises with time requiring flow of solute atoms from outer regions, so the next  $c$ -well is created, and so on. Thus the wave-like concentration distribution spreads over the crystal with the characteristic Cahn wavelength  $\lambda_c$ , while its front replicates the form of the initial APB. Later on the usual coarsening process starts, by splitting or fusion of some of stripes and evaporation of smaller precipitates.

Looking for experimental manifestations of APB replication, one should take into account thermal fluctuations of local occupations  $n_i$  which are neglected in MFA. Such fluctuations can induce homogeneous spinodal decomposition competing with the APB replication. To simulate the effects of fluctuations we introduced additional small random fluctuations immediately after annealing, i.e. at  $t' = 0$ . The results are illustrated in Fig. 6. To facilitate the comparison with experimental dark-field micrographs, the colour code has been changed with respect to all other figures of this paper, as described in the Figure 6 caption. The simulated microstructures reveal great similarity with the observed ones<sup>11,13</sup>. In particular, the ordered layer adjacent to APB in Fig. 6 (the

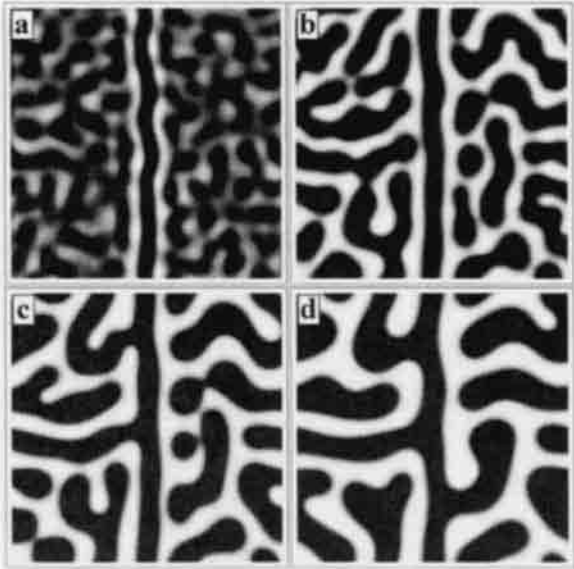


Fig. 6. Same as in Fig. 5 but with random fluctuations introduced after the second quench (see text) near the straight APB, at following  $t'$ : (a) 100, (b) 500, (c) 1000, and (d) 2000. The grey level varies linearly with the degree of order, from the completely dark for the most disordered region, to the completely white for the most ordered one.



Fig. 7. Dark-field micrographs from Ref.<sup>13</sup> for the Ni-0.247 Al alloy after the two-step quench, first to  $T_a = 903$  K, and then to  $T = 843$  K (which supposedly corresponds to areas  $b$  and  $d$ , respectively, in Fig. 1), at following times  $t$  after the second quench (in minutes): (a) 0, (b) 10, (c) 100, (d) 1000, and (e) 10000.

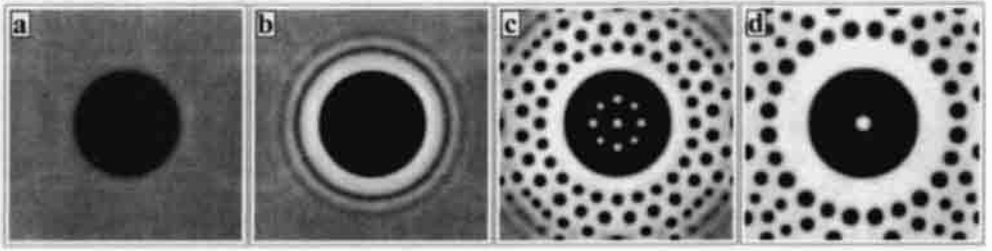


Fig. 8. Temporal evolution of  $c_i$  for the alloy model described in text after the quench from  $T'_a = 0.9$  to  $T' = 0.61$ , at following times  $t'$  after the quench: (a) 0, (b) 120, (c) 260, and (d) 1000.

above-mentioned  $c$ -bank) is also distinctly seen in micrographs (b) and (c) in Fig. 7. Later on the nearby disordered precipitates begin to fuse with the APB, forming dark "branches" almost normal to the APB "trunk" (Figs. 6c and 6d), which is also clearly seen in micrographs 7(c) and 7(d). Let us also note that the previous experiments<sup>11,13</sup> have been performed just near the conditional spinodal in the  $c, T$  plane, while with moving away from the spinodal curve replica'ion effects should get more pronounced<sup>5</sup>.

#### 4. Replication of interphase boundaries under spinodal decomposition

Another kinetic phenomenon where Cahn's critical waves can possibly be visualized and studied is the replication of interphase boundaries (IPB) illustrated in Figs. 8-10. Similarly to the replication of APBs, it can arise after a two-step quench of an initially uniform disordered alloy. First the alloy is quenched and annealed at temperature  $T_a$  in some two-phase state that can be either metastable or spinodally unstable with respect to phase separation. Varying the annealing time  $t_a$  one can grow here precipitates ("droplets") of a suitable size  $l$ . For sufficiently large  $l$ , the concentration  $c(\mathbf{r})$  within A-riched droplets is close to the equilibrium binodal value  $c_b(T_a)$  (thin curve in Fig. 9).

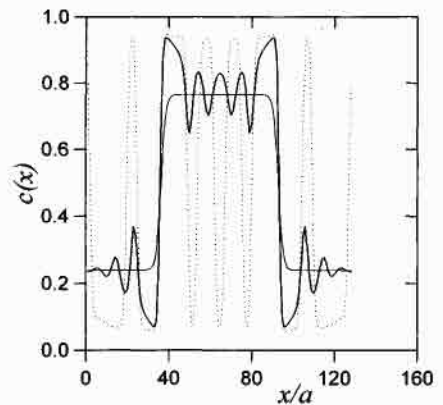


Fig. 9. Concentration profiles for alloy states shown in Fig. 8. Thin, thick and dotted curve correspond to states (a), (b), and (c), respectively.

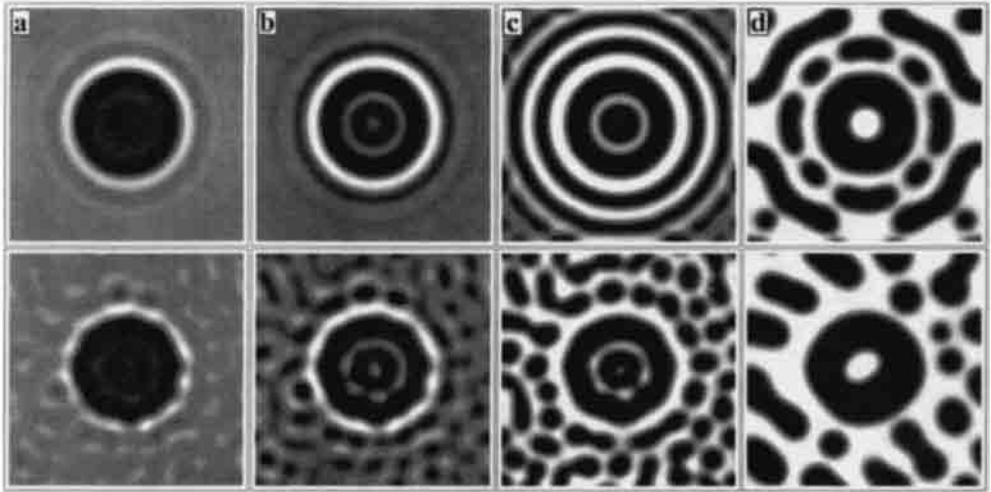


Fig. 10. Upper row: same as in Fig. 8, but at  $T_a = 0.995$ ,  $T' = 0.9$  and following  $t'$ : (a) 400, (b) 600, (c) 1000, and (d) 5400. Lower row: same as in upper row, but with random fluctuations introduced after the quench, see text.

Then the mixture with droplets is quenched into the spinodal instability region to some  $T < T_a$ . Concentration  $c(\mathbf{r})$  within droplets starts to evolve towards the value  $c_b(T) > c_b(T_a)$ , but the evolution type depends crucially on the value  $\Delta c_b = c_b(T) - c_b(T_a)$ . At small  $\Delta c_b$  we have a usual diffusion with smooth changes of composition in space and time. But when  $\Delta c_b$  is not small (for our simulations:  $\Delta c_b \gtrsim 0.2$ ), evolution is realised via peculiar wave-like patterning shown in Figs. 8-10.

To examine replication of IPBs we made MFKE-based simulations using the simplest 2D alloy model with the nearest-neighbor interaction. Some results are presented in Figs. 8-10. The lower row in Fig. 10 illustrates possible effects of thermal fluctuations, similar to those discussed in Sec. 3 for the replication of APBs. The figure shows that peculiar features of microstructural evolution are preserved even under rather strong thermal fluctuations used in this simulation.

## 5. Vacancy segregation at interphase and antiphase boundaries

The problem of taking into consideration the actual vacancy-mediated atomic exchange mechanism (rather than the direct exchange model used in most theoretical treatments) recently received some attention. In particular, possible presence of vacancy segregation at various structural inhomogeneities was discussed. However, the estimates of these effects by various authors disagree notably with each other<sup>14,15</sup>, and there seems to be no general treatment of this problem available.

We studied vacancy segregation near interphase and antiphase boundaries using the MFA and PCA approaches described in Sec. 6 below. For the A-B alloy with vacancies, the stationary distribution of mean vacancy occupations  $c_i^v = \langle n_i^v \rangle$  can be explicitly written out in terms of the main component distribution,  $c_i^A = c_i$  and  $c_i^B \simeq 1 - c_i = c_i^C$ . In particular, the PCA expression for  $c_i^v$  is

$$c_i^v = Const \cdot c_i^A \prod_j \left\{ 1 + \frac{2c_j^v(f_{ij} + 1)f_{ij}^P}{1 + R_{ij} + f_{ij}(c_i^A + c_j^A)} \right\} \quad (14)$$

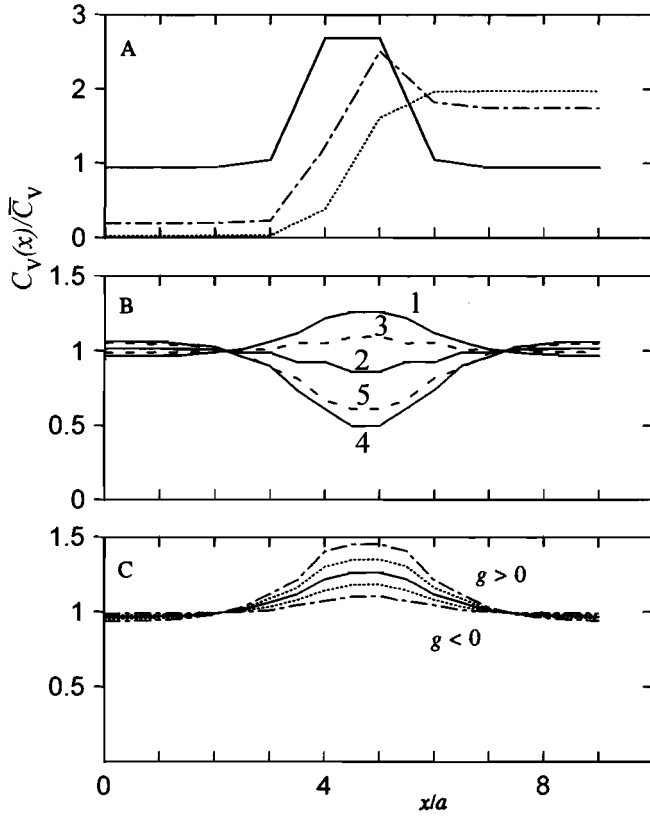


Fig. 11. (A) Vacancy profiles near the (1,0,0) interphase boundary for the BCC alloy model with the nearest neighbor interaction:  $v_{ij} = v_1 = -1$  and the preference potential  $P_{ij} = gv_{ij}$ , at  $T' = 0.5$  and following  $g$ : solid curve,  $g = 0$ ; dot-dashed curve,  $g = 0.5$ ; dotted curve,  $g = 1$ . (B) Vacancy profiles near the (1,0,0) antiphase boundary for the B2 order in the BCC alloy with two-neighbor interactions:  $v_1 = 1$ ,  $v_2 = -0.8$ ,  $P_{ij} = gv_{ij}$ , at  $T' = 0.75$ ,  $c = 0.4$ , and following  $g$ : curve 1,  $g = 0$ ; curve 2,  $g = 1$ ; curve 3,  $g = -1$ ; curve 4,  $g = 2$ ; curve 5,  $g = -2$ . (C) Same as in (B), but at  $P_{ij} = g|v_{ij}|$ , and following  $g$ : solid curve,  $g = 0$ ; dotted curve,  $g = \pm 1$ ; dot-dashed curve,  $g = \pm 2$ .

Here  $Const$  is determined by boundary conditions,  $f_{ij} = \exp(-\beta v_{ij}) - 1$ ,  $f_{ij}^P = \exp[\beta(v_{ij} + P_{ij})/2] - 1$ , the "preference potential"  $P_{ij} = 2(V_{ij}^{Bv} - V_{ij}^{Av}) + V_{ij}^{AA} - V_{ij}^{BB}$  describes attraction of vacancies to A- or B-rich domains, and  $R_{ij}$  is given by Eq. (19) below.

The general expressions have been applied to study vacancy distributions near plane IPB and APB. Some of our PCA results are presented in Fig. 11, where  $c_v^i = c_v(x_i)$  is given in reduced units  $c_v(x)/\bar{c}_v$  with  $\bar{c}_v = [c_v(\infty) + c_v(-\infty)]/2$ . The figure shows, in particular, that the preference potential can significantly affect the vacancy segregation. For example, near IPB (fig. 11, A) the segregation is present only at not large  $|P_{ij}| \lesssim |v_{ij}|$ . Near APB (Fig. 11, B), the significant preference potential can even invert segregation to depletion, depending also on the composition  $c$ . All these effects are explained by the free energy minimum considerations for IPB or APB in the presence of vacancies.

In Fig. 12 we present some results of MFKE-based simulation of spinodal decomposition with the vacancy-mediated exchange mechanism. We use the same 2D model on a square lattice with the nearest-neighbor interaction and  $P_{ij} = 0$  as in Refs.<sup>14,15</sup>,

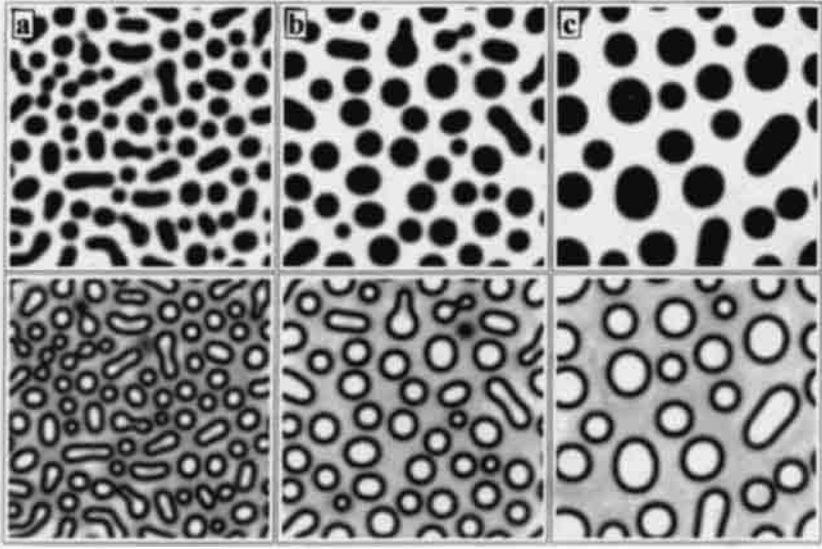


Fig. 12. Temporal evolution of  $c_i = c_i^A$  (upper row) and  $c_i^B$  (lower row) for the alloy model described in text, at  $T' = 0.4$ ,  $c = 0.35$ ,  $\bar{c}_v = 0.01$ , and following values of the reduced time  $t^* = t\bar{c}_v\gamma_{Av}$  after the quench: (a) 1100, (b) 4300, and (c) 18000.

supposing vacancies to exchange with neighboring A or B atom with equal probabilities  $\gamma_{Av} = \gamma_{Bv}$ . Fig. 12 demonstrates the pronounced vacancy segregation at IPBs. It also illustrates sharp changes of local vacancy distributions under fusion or evaporation of the precipitates. However, general features of evolution for main alloy components, A and B, seem to remain similar to those for the direct exchange model, see e.g. Fig. 3. Therefore, the effect of the vacancy-mediated exchange in this case reduces mainly to the rescaling of time for the microstructural evolution.

## 6. Exact and approximate relations for free energy of a nonuniform alloy

In this Section we use Eqs. (2)-(10) to derive several relations for the free energy  $F\{c_i\}$  of a stationary nonuniform alloy. These relations can be used to study properties of interphase and antiphase boundaries, nucleation problems, etc.

When interactions  $v_{ij}$  in a binary alloy are purely pairwise, i.e. the rhs of Eq. (4) includes only the first term, one can derive an exact relation between  $F\{c_i\}$  and its derivatives over  $c_i$ . Firstly we note that according to Eqs. (2)-(6) the fluctuation correlator  $K_{ij} = \langle (n_i - c_i)(n_j - c_j) \rangle$  is related to the free energy as

$$(\hat{K}^{-1})_{ij} = \beta \partial^2 F / \partial c_i \partial c_j \quad (15)$$

where  $\hat{K}^{-1}$  is the matrix inverse to  $(\hat{K})_{ij} = K_{ij}$ . Let us consider Hamiltonians  $H(g)$  that depend on the auxiliary charge variable  $g$  and correspond to substitution of  $v_{ij}$  in Eq. (4) by  $gv_{ij}$ , with  $g = 1$  for the actual system. Then, using the "differentiating over charge" method, we obtain the following relation

$$F\{c_i, g\} = T \sum_i (c_i \ln c_i + c'_i \ln c'_i) + g \sum_{i>j} v_{ij} c_i c_j + \sum_{i>j} v_{ij} \int_0^g dg' K_{ij}\{c_i, g'\} \quad (16)$$

Eqs. (15) and (16) form an exact and explicit set of equations for  $F\{c_i, g\}$ .



These equations can also be used for approximate calculations of  $F\{c_i\}$ . The simplest approximation is MFA that neglects all statistical fluctuations and correlations. Therefore, the MFA expression  $F_{\text{MFA}}$  given by Eq. (13) corresponds to the omission of the last term in Eq. (16).

Taking into account the fluctuative contribution as the perturbative correction, i.e. using for  $K_{ij}$  in Eq. (16) the relation (15) with  $F = F_{\text{MFA}}$ , we obtain the "MFA with fluctuative correction" expression,  $F_{\text{MFA+f}}$ :

$$F_{\text{MFA+f}} = F_{\text{MFA}} + F_{\text{If}}; \quad F_{\text{If}}\{c_i\} = T \frac{1}{2} \text{Tr} \ln(1 + \beta \hat{v} \hat{z}) \quad (17)$$

Here  $(\hat{v})_{ij} = v_{ij}$ ,  $(\hat{z})_{ij} = \delta_{ij} c_i c'_i$ , and  $\text{Tr} \hat{A} = \sum_i A_{ii}$ . Eq. (17) generalises the analogous expression for homogeneous systems<sup>16</sup> to the nonuniform case.

Calculations for uniform systems showed that the perturbative treatment usually overestimates the fluctuative contribution<sup>16</sup>. Thus more refined, cluster methods have been developed, such as the CVM and CFM<sup>10</sup>. They can be extended to nonuniform systems. In particular, the pair cluster (PCA) expression for  $F\{c_i\}$  can be written out analytically<sup>10</sup>:

$$\beta F_{\text{PCA}}\{c_i\} = \sum_i (c_i \ln c_i + c'_i \ln c'_i) + \sum_{ij} c_i \ln(1 - c_j g_{ij}) - \sum_{i>j} \ln(1 - c_i c_j g_{ij}) \quad (18)$$

Here  $g_{ij} = 2f_{ij}/[R_{ij} + 1 + f_{ij}(c_i + c_j)]$ ,  $f_{ij}$  is the same as in Eq. (14), and

$$R_{ij} = [1 + 2f_{ij}(c_i c'_j + c'_i c_j) + f_{ij}^2 (c_i - c_j)^2]^{1/2} \quad (19)$$

We can also use Eq. (16) to refine the description of fluctuative effects in PCA employing for  $K_{ij}$  in this equation the PCA result  $K_{ij}^{\text{PCA}}$  which corresponds to the substitution of  $F_{\text{PCA}}$  into Eq. (15):

$$F_{\text{PCA+f}}\{c_i\} = T \sum_i (c_i \ln c_i + c'_i \ln c'_i) + \sum_{i>j} v_{ij} c_i c_j + \sum_{i>j} v_{ij} \int_0^1 dg K_{ij}^{\text{PCA}}\{c_i, g\} \quad (20)$$

Applications of Eqs. (17)-(19) to concrete problems show that when the fluctuative effects are important (as in the nucleation problem treated in Sec. 7), the "PCA+f" approximation can be notably more accurate than the lower ones, (17), (13) and (18), while the PCA and MFA results usually do not greatly differ with each other.

## 7. Microscopic theory of nucleation in metastable alloy states

Development of the theory of nucleation is the long-standing problem in the statistical physics. The kinetic approach to this problem was proposed by Zeldovich<sup>17</sup>. For the nucleation rate  $J$ , i.e. for the number of critical and supercritical embryos being formed in the unit volume per unit time at early stages of nucleation, he obtained the following expression

$$J = J_0 \exp(-\beta \Delta \Omega) \quad (21)$$

Here the nucleation barrier  $\Delta \Omega$  is the excess thermodynamic potential needed to form the critical embryo within the uniform metastable state, while the prefactor  $J_0$  is determined by the kinetic characteristics for the embryo diffusion in the space of its size  $a$ . Expressions for both  $\Delta \Omega$  and  $J_0$  given by Zeldovich include a number of phenomenological parameters.

Later on Cahn and Hilliard<sup>18</sup> presented some thermodynamic estimates for the nucleation of liquid in vapour. Values of  $\Delta \Omega$  and the composition profiles  $c(r)$  of the embryos have been estimated using the mean-field and gradient expansion approximations for the free energy functional  $F\{c(r)\}$ . A number of qualitative features in variation



of both  $\Delta\Omega$  and  $c(r)$  with supersaturation has been found; in particular, the diffuse character of the embryo interface with the exterior phase has been noted. However, no kinetic treatment and estimates for alloys have been presented.

The present work aims to derive fully microscopic expressions for the nucleation rate  $J$  and to apply the results to realistic estimates of nucleation rates in alloys. We suppose that the state with a critical embryo obeys the local stationarity conditions (9):  $\partial F/\partial c_i = \mu$ , but is unstable, i.e. corresponds to the saddle point  $\{c_i^s\}$  of the function  $\Omega\{c_i\} = F\{c_i\} - \mu N$  in the  $c_i$ -space<sup>18</sup>. At small  $\delta c_i = c_i - c_i^s$  we have

$$\delta\Omega = \Omega\{c_i\} - \Omega\{c_i^s\} = \frac{1}{2} \sum_{ij} F_{ij} \delta c_i \delta c_j \quad (22)$$

where  $F_{ij} = \partial^2 F/\partial c_i \partial c_j$ . Diagonalizing the rhs of Eq. (22) with the unitary transformation  $\delta u_k = \sum_i A_{ki} \delta c_i$ , we obtain

$$\delta\Omega = \frac{1}{2} \sum_{k=0} \gamma_k (\delta u_k)^2 \quad (23)$$

where  $\gamma_k$  are the eigenvalues of the matrix  $F_{ij}$ . The instability implies that the lowest eigenvalue  $\gamma_0$  is negative, while the relevant variable  $u_0$  corresponds to the embryo size  $a$ . There are also three next eigenvalues,  $\gamma_1$ ,  $\gamma_2$  and  $\gamma_3$ , that correspond to the translation of the embryo, while variables  $u_1$ ,  $u_2$  and  $u_3$  describe its position  $\mathbf{r}$ . For actual large embryos the translation is virtually barrierless: values  $|\beta\gamma_{1,2,3}|$  are of the order or less than  $10^{-4}$  and can be neglected.

The probability  $dw(a, \mathbf{r})$  to find an embryo of size  $a$  with its center at point  $\mathbf{r}$  within the metastable state (treated as the equilibrium one<sup>17</sup>) is related to the distribution function  $f(a, \mathbf{r})$  as

$$dw(a, \mathbf{r}) = f(a, \mathbf{r}) da d^3r, \quad (24)$$

and the microscopic expression for  $f(a, \mathbf{r})$  for large embryos under consideration is

$$f(a, \mathbf{r}) = \sum_{\{n_i\}} \exp[\beta(\Omega + \mu \sum_i n_i - H)] \prod_{\alpha=0}^3 \delta(u_\alpha - \sum_i A_{\alpha i} n_i) D_{\mathbf{r}}(\mathbf{u}) \quad (25)$$

where  $D_{\mathbf{r}}(\mathbf{u})$  is the Jacobian  $D(u_1, u_2, u_3)/D(x, y, z)$ .

After certain manipulations, the rhs of Eq. (25) can be reduced to the free energy  $F\{c_i\}$  for a certain nonuniform alloy and can be calculated using the methods mentioned in Sec. 6. Similar microscopic treatment can be performed for the embryo diffusion kinetics in the  $a$ -space.

The resulting expression for the nucleation rate  $J$  has the Zeldovich-Volmer form (21) where  $\Delta\Omega$  is the difference  $\Omega\{c_i^s\} - \Omega_0$  with  $\Omega\{c_i^s\} = F\{c_i^s\} - \mu N$  calculated at fixed values of variables  $a = u_0^s$  and  $\mathbf{u} = \mathbf{u}(\mathbf{r})$ . The microscopic expression for the prefactor  $J_0$  is

$$J_0 = (\beta|\gamma_0|/2\pi)^{1/2} D_{aa} \mathcal{N} D_{\mathbf{r}}(\mathbf{u}) \quad (26)$$

Here  $D_{aa}$  is the embryo diffusivity in the space of sizes  $a$ , while the factor  $\mathcal{N}$  is the normalizing constant for the distribution function  $f(a, \mathbf{r})$ :

$$D_{aa} = \sum_{ij} A_{0i} (\delta_{ij} \sum_l M_{il} - M_{ij}) A_{0j}, \quad \mathcal{N} = \prod_{\alpha=0}^3 (2\pi z_{\alpha\alpha})^{-1/2}, \quad (27)$$

the mobility  $M_{ij}$  is the same as in Eq. (11),  $z_{\alpha\alpha} = \sum_{ij} A_{\alpha i} z_{ij} A_{\alpha j}$ , and  $z_{ij} = \delta_{ij} c_i c_j'$ .

Application of Eqs. (21)–(27) to the calculations of the nucleation rates  $J$  for various alloy models revealed a number of interesting results, in particular, sharp dependence of  $J$  and embryo characteristics on the supersaturation, temperature, interaction radius, etc. These results will be described elsewhere.

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## TOTAL ENERGY CALCULATIONS OF ALLOYS: LOCALLY SELF-CONSISTENT GREEN'S FUNCTION METHOD

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There is a growing interest in first-principles investigations of materials with broken translational symmetry, for example, impurities, interfaces, and alloys. In particular, the total energy and the electronic structure calculations of systems with an arbitrary distribution of atoms on an underlying lattice will give information essential to understanding their stability and properties. At the same time two schemes most frequently used in *ab initio* total energy calculations for completely random alloys, the Connolly-Williams (CW) method<sup>1</sup> and the methods based on the single-site approximation, as the coherent potential approximation (CPA)<sup>2</sup>, have limited applicability and reliability<sup>3</sup>. Another way of approaching the solution to the electronic structure problem for disordered systems is given by the supercell technique. In this case the three-dimensional periodicity is restored although its effect on the final result can be neglected. Then conventional band structure methods can be used. However, this approach has both fundamental and technical limitations. For instance, from the basic point of view all details connected with the smearing of the electronic spectrum and the Fermi surface in alloys are lost. From the technical point of view the computational effort increases as  $N^3$  with increasing number of atoms  $N$  in the supercell.

To improve the latter a number of  $O(N)$  methods have been recently proposed but practically all of them exploit Hamiltonian formalism. However, in Refs. 4,5 the locally self-consistent multiple scattering (LSMS) method based on the real space multiple scattering theory has been outlined, and in Ref. 6 its central idea in the form of the local interaction zone (LIZ) was incorporated into the Green's function technique, leading to the locally self-consistent Green's function method (LSGF).

Let us give a brief summary of the LSGF method. We will consider a system of  $N$  atoms somehow distributed on the underlying primitive lattice. We start with the notion that if we choose an unperturbed reference system which has an ideal periodicity by placing equivalent effective scatterers on the same underlying lattice, its Hamiltonian  $H^U$  may be calculated in the reciprocal space. Corresponding unperturbed Green's

function  $G^U = (E - H^U)^{-1}$  may then be calculated, and transformed to the real space by integration over the Brillouin zone. The Green's function for the perturbed system with broken periodicity  $G^P$  is connected to the unperturbed Green's function by the Dyson equation

$$G^P = G^U + G^U(H^P - H^U)G^P, \quad (1)$$

where the Hamiltonians for the perturbed system  $H^P$ , as well as for the unperturbed system, are calculated in the real space. There are two cases when eq. (1) can be used for practical applications. Firstly, if the perturbation  $\Delta = H^P - H^U$  is localized (though not necessarily small !) it reduces to the finite size matrix problem. This case occurs for the impurity problem or for an interface. Secondly, the finite size problem may appear if one (or both) Green's functions in (1) are short ranged. Normally this is not the case for  $G^P$ . Therefore it is highly desirable to choose the reference unperturbed system which has localized real space Green's function. To simplify the solution of eq. (1) it is also desirable to make the difference of two Hamiltonians  $\Delta$  as small as possible, which means that effective scatterers should describe the properties of real atoms on the average as reliable as possible. However, we do not require the effective medium to reproduce the properties of the initial system on the average exactly because the short range character of its Green's function will make the size of the matrices finite anyway. In addition, we require the effective medium to be as simple as possible, i.e. the single-site.

As a matter of fact there is an infinite number of possible choices for the effective medium. But if one deals with an alloy problem, it is well-known that the best single-site effective medium is given by the CPA<sup>2</sup>. In fact, it fulfills all the criteria mentioned above. That is, the Green's function for the CPA effective medium decays, apart from an oscillating factor, exponentially as  $R^{-1}e^{-R/l}$ , where  $l$  is the mean free path, and gives very good average density of states, as has been shown in a number of applications. However, though our system may be composed of the atoms of, say, two types, A and B, all the  $N$  atoms will be, in general, different due to the different local environments they have got. This difference is totally ignored in two component CPA, but may be accounted for to some extent (restricted by the single-site approximation) in the framework of the multi-component generalization<sup>7</sup>. Therefore, we will define the effective medium to be used in eq. (1) as one given by the CPA for a multi-component alloy with total number of components  $N$ , and we will refer to our method with this particular choice of the effective medium as the LSGF-CPA method. To determine the potential function for effective atoms and the effective medium Green's function one must therefore solve the system of coupled single-site equations

$$\begin{aligned} \tilde{g}_{RR} &= (V_{BZ})^{-1} \int_{BZ} d\mathbf{k} ([\tilde{P} - S(\mathbf{k})]^{-1})_{RR} \\ g_R^0 &= \tilde{g}_{RR} + \tilde{g}_{RR}(\tilde{P}_R - P_R)g_R^0 \\ \tilde{g}_{RR} &= \langle g_R^0 \rangle = (N)^{-1} \sum_{R=1}^N g_R^0, \end{aligned} \quad (2)$$

where  $S(\mathbf{k})$  is the TB-LMTO structure constant matrix for the primitive lattice and  $V_{BZ}$  the volume of the corresponding Brillouin zone,  $P$  is the LMTO potential function,  $g$  is the so-called KKR-ASA Green's function,  $R$  denote lattice sites, tilde refers to the effective medium, and the explicit dependences on the (complex) energy  $z$  and combined angular-momentum quantum number  $L = (l, m)$  are omitted.

When the properties of the effective scatterers are determined, i.e. the reference system is defined, we solve eq. (1). However, the experience gained in applications

of real-space cluster methods to electronic structure calculations shows that for large clusters the properties of atoms deep inside are very close to those given by band structure schemes. This suggests that the electronic density and the density of states on a particular atom within a large condensed system can be obtained with sufficient accuracy by considering only the electronic multiple scattering processes in a finite spatial region centered at that atom. So, instead of direct solution of eq. (1) we have employed the local interaction zone (LIZ) concept of Ref. 4,5. Within this concept each atom of the original system is surrounded by  $M - 1$  nearest neighbors forming the  $M$ -atomic LIZ. Each LIZ is then embedded into the effective medium, and the Green's function *at the central site* is calculated by the impurity cluster Dyson equation, thus providing us the Green's function at this site which is locally self-consistent:

$$g_{RR} = \tilde{g}_{RR} + \sum_{R'=1}^M \tilde{g}_{RR'}(\tilde{P}_{R'} - P_{R'})g_{R'R}. \quad (3)$$

Here  $R, R' \in LIZ$ , and the effective medium Green's function for the LIZ  $\tilde{g}_{RR'}$  is calculated only once for the entire system

$$\tilde{g}_{RR'} = (V_{BZ})^{-1} \int_{BZ} d\mathbf{k} e^{i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} [\tilde{P} - S(\mathbf{k})]^{-1}. \quad (4)$$

Thereby the solution of the electronic-structure problem for an  $N$ -atomic system is decomposed into  $N$  locally self-consistent problems including only the  $M$  atoms in the LIZ associated with each atom in the system, and the computational effort now scales linearly with  $N$ , i.e. exhibits  $O(N)$  scaling.

We would like to assert that we did not introduce any approximations within the local interaction zone concept because it is based on the solution of the exact Dyson equation. Of course, strictly speaking one has to consider the LIZ of infinite size. But actually the application of a judiciously chosen effective medium leads to a minimal size of the local interaction zone. Really, one immediately observes from eq. (3) that although the off-diagonal blocks of the desired Green's function matrix  $g_{RR'}$  may be long-ranged this becomes irrelevant for the on-site matrix element if an effective medium can be found such that  $\tilde{g}_{RR'}$  has short range in which case the sum over lattice sites may be restricted to a finite cluster, i.e. a local interaction zone containing  $M$  atoms.

When  $g_{RR}$  is known for all atoms in the system we calculate the density of states (DOS) at all the sites and find new charge densities by integration of the DOS up to the Fermi energy  $E_F$ . The total energy and the new potentials are then calculated in the atomic sphere approximation. In particular, the Madelung contribution to the one-electron energy and potential may be calculated by imposing the periodic boundary conditions on the original  $N$  atomic system. The whole scheme starting with the determination of  $\tilde{P}$  is then repeated until the self-consistent potential and total energy are obtained.

In order to illustrate the possibility to calculate accurately the total energies for systems with any distribution of atoms on the underlying lattice within LSGF-CPA method we have performed self-consistent calculations for the fcc  $\text{Rh}_{50}\text{Pd}_{50}$  alloy with three different atomic configurations: completely ordered in the  $L1_0$  structure, completely random, and segregated. We have considered a supercell with 144 atomic sites and with periodic boundary conditions. The atomic distributions are shown in Fig. 1. The degree of order may be characterized by the Warren-Cowley short-range order parameters  $\alpha_i$  where  $i$  is the number of the neighboring shell. In setting up a particular atomic distribution we took care of  $\alpha_i$  for  $i \leq 5$ . In the  $L1_0$  structure (Fig. 1, top panel)  $\alpha_i = -1/3$  and 1 for the odd and even shell numbers, respectively. The random

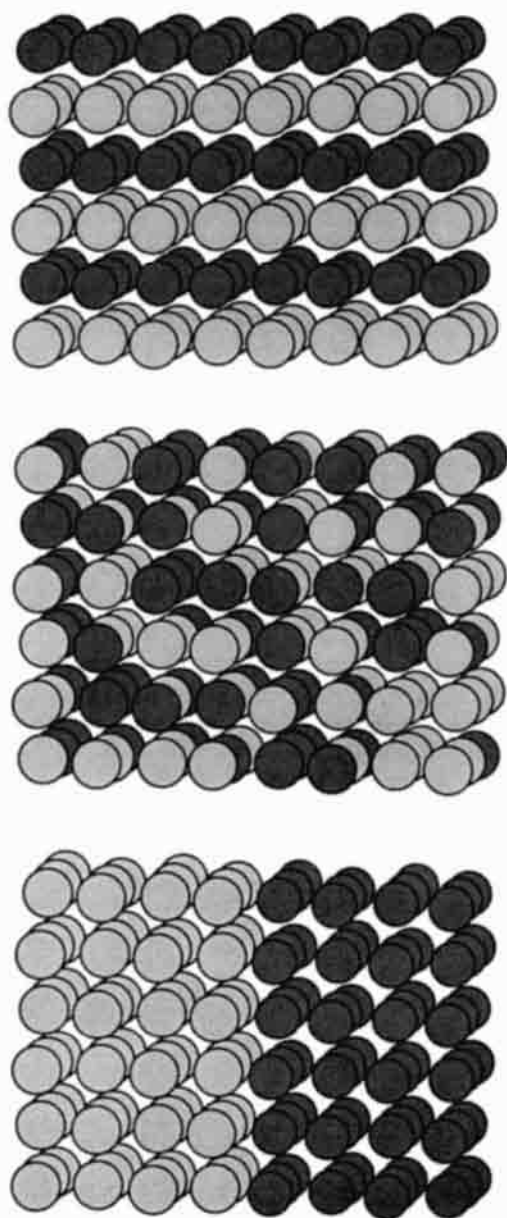


**Figure 1.** Three different distributions of Rh (dark gray) and Pd (light gray) atoms in equiatomic fcc Rh-Pd alloy. The ordered sample ( $L1_0$  structure, top), the random sample (middle), and the segregated sample (bottom) were constructed on the fcc underlying lattice for the 144 atomic supercell.

sample (Fig. 1, middle panel) was constructed with  $\alpha_i = 0$  for  $i$  from 1 to 5, and for the segregated sample (Fig.1, bottom panel)  $\alpha_i$  were positive up to the fifth shell. The results of the LSGF-CPA calculations were compared with those of the conventional LMTO method for ordered sample, as well as with LMTO-CPA results for the random alloy ( we expect the CPA to give reliable total energies for Rh-Pd alloy because charge transfer in this system is very small). Finally, one can see in Fig. 1 that the segregated sample is built up of alternating (010) layers of pure Rh and Pd, so its total energy can be calculated, besides using the LSGF method, by the interface Green's function technique<sup>8</sup> (interface GF).

In Fig. 2 we show the total energies of the three samples as a function of the number of neighboring shells included in the LIZ. In agreement with the experimental phase diagram for the Rh-Pd system which is a case with phase separation, we find the segregated sample to have the lowest total energy. Next comes the random alloy, and the ordered phase has the highest total energy. The excellent real-space convergence of the LSGF-CPA method may be also judged from Fig. 2. That is, already for the LIZ which includes just one shell of the nearest neighbors (i.e. 13 atoms) the total energies are converged to about 0.5 mRy, and for four shells the difference between LSGF method and the reference calculations (bulk LMTO and interface Green's function technique) is below 0.1 mRy. The difference between the LSGF and CPA calculations is expected to be larger, and as a matter of fact one must judge the accuracy of the latter rather than the former from this comparison.

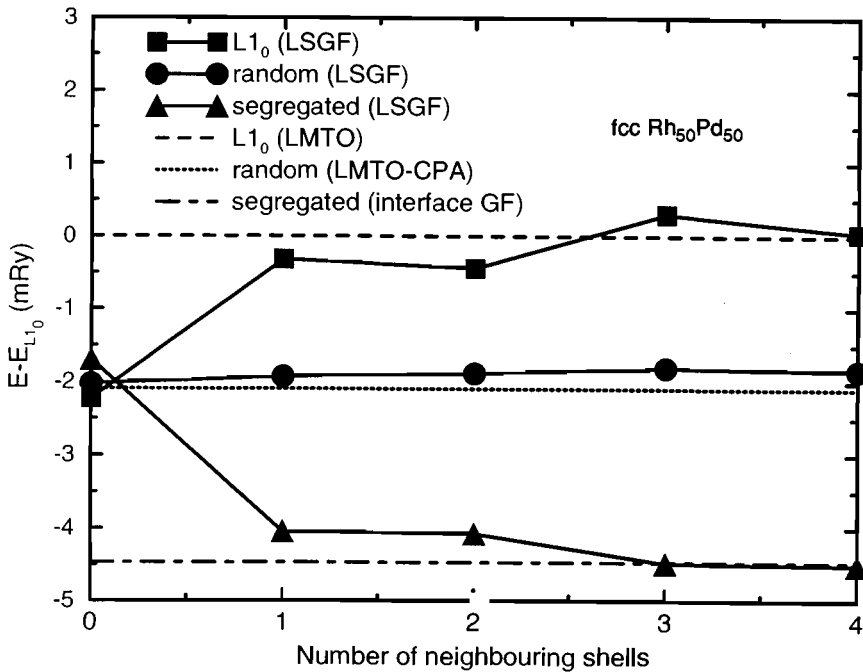


**Figure 2.** Total energies of ordered ( $L1_0$  structure, squares), random (circles) and segregated (triangles) fcc  $Rh_{50}Pd_{50}$  alloys as a function of the number of neighboring shells included in the local interaction zone. Values obtained by the LSGF-CPA method are shown by filled symbols and full lines. The energies obtained by the reference calculations are shown by a dashed line (LMTO, ordered sample), a dotted line (LMTO-CPA, random sample), and a dot-dashed line (interface Green's function technique, segregated sample).

We remark here that within the LSGF method we have obtained reliable total energies for systems which otherwise should be treated by means of three different techniques. Moreover, the LSGF method allows one to consider *any* atomic distribution on the underlying lattice, and thereby to obtain electronic properties like the total energy or the density of states by direct solution of the electronic structure problem. As an example, in Ref. 6 we have calculated mixing enthalpies of fcc Cu-Zn alloys with short-range order and obtained very good agreement with experiment.

In summary, we have outlined a new method for the first-principles investigations of the electronic properties of systems with broken three-dimensional periodicity, the LSGF method. It has order  $N$  scaling when the system size is increased. We have applied it for the calculations of the total energies of the fcc Rh<sub>50</sub>Pd<sub>50</sub> alloy with different degrees of order, and obtained excellent agreement with other first-principles techniques. We conclude that the LSGF method gives a reliable description of the electronic properties of systems with arbitrary atomic distribution on the underlying crystal lattice.

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# ROUGHENING OF AN ANTIPHASE BOUNDARY NEAR A BULK FIRST ORDER TRANSITION

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## INTRODUCTION.

An ordering phase transition is characterized by a loss of symmetry: the ordered phase has less symmetry than the disordered one. Hence, an ordering process leads to the coexistence of different domains of the same ordered phase. An interface forms whenever two such domains contact. The thermodynamic behavior of this interface is governed by different forces. The presence of the underlying lattice and the stability of the ordered domains tend to localize the interface and to reduce its width. On the other hand, thermal fluctuations favor an interfacial wandering and an increase of the interface width. The result of this competition depends strongly on the order of the bulk phase transition.

When the bulk order-disorder transition is of second order, general arguments based on dimensionality show that the interface generally displays a two-dimensional phase transition at a *roughening* temperature  $T_R$  less than the bulk order-disorder transition temperature  $T_c$ . Below  $T_R$ , the interface is smooth and localized: its width is of the order of the bulk correlation length. Above  $T_R$ , the interface wanders through the lattice and gets delocalized. Its width increases logarithmically with its transverse size. Many situations that belong to this category have already been investigated<sup>[1-4]</sup>.

When the bulk transition is of first order, the above mentioned arguments based on dimensionality do not apply and the *would be* roughening transition temperature  $T_R$  may be larger than the bulk transition temperature  $T_c$ , in which case there is simply no roughening transition. The situation is further complicated by the wetting phenomena. When we approach  $T_c$  from below, the disordered phase becomes metastable and may wet the interface: a large layer of disordered phase develops in between the two ordered domains.

The aim of the present study is precisely to investigate the thermodynamical properties of an interface when the bulk transition is of first order. We will consider the case of a binary alloy on the fcc lattice which orders according to the  $L1_2$  ( $\text{Cu}_3\text{Au}$  type) structure.

## MODEL AND PRELIMINARIES

We assume an Ising-like Hamiltonian of the form

$$H = J_1 \sum_{\langle nn \rangle} \sigma_i \sigma_j + J_2 \sum_{\langle nnn \rangle} \sigma_i \sigma_j - h \sum \sigma_i$$

where the first (second) sum runs over the first (second) neighbour sites. The spin variable  $\sigma_n$  takes values  $\pm 1$  depending on whether site  $n$  is occupied by an A or by a B atom. The magnetic field  $h$  represents the difference between the chemical potentials of the two atomic species. For our calculations, we have considered  $J_1=50$  meV,  $J_2=-10$  meV and  $h=400$  meV [we express energies in meV and temperatures in Kelvin]. In that case, the bulk order-disorder transition between the  $L1_2$  phase and the disordered one takes place at  $T_b=1690 \pm 2$  K.

The fcc lattice may be splitted into four simple cubic sublattices. In  $L1_2$ , one simple cubic sublattice is occupied by B atoms and the three others by A atoms [see Fig. 1]. The contact between two different ordered domains lead either to a conservative antiphase boundary (APB) or to a non-conservative one, depending on whether the concentration at the APB is the same as that of the bulk or not <sup>1</sup>. In the following, we consider the case of a non-conservative APB along the (100) direction, *i.e.* we assume that the minority atoms principally occupy sublattice 1 for the ordered domain on the left of the APB and the sublattice 4 for the ordered domain on the right [see Fig. 2]. We perform our simulations on 3-dimensional systems of dimensions  $L_\perp$  along the X-axis and  $L_\parallel$  along the Y and Z-axis (in unit of fcc cubes). We impose a non-conservative APB perpendicular to the X-axis and use periodic boundary conditions along Y and Z and fixed boundary conditions along X [ $L_\perp$  will be fixed to 24, which is large enough to avoid finite size effects and any influence of the fixed boundary conditions perpendicular to the APB, except close to the bulk transition temperature, where we used  $L_\perp=60$ ].

The thermodynamical properties of the APB will be investigated through the behavior of some local order parameter defined for each fcc cube having co-ordinates  $\{x,y,z\} \equiv R$  in a given MonteCarlo (MC) configuration  $C$  as:

$$\eta_C(R) = 1/2[\sigma_1^C(R) - \sigma_2^C(R) + \sigma_3^C(R) - \sigma_4^C(R)]$$

where  $\sigma_\alpha^C(R)$  denotes for a given configuration  $C$ , the spin occupying the  $\alpha$ -th sublattice of the unit cube located at  $R$ . This order parameter permits to distinguish between the two-ordered domains and the APB. As example, at zero temperature, a fcc cube that belongs to ordered domains will be characterized by  $-1$  or  $+1$  (for right and left domains, respectively, in Fig. 1), whereas the order parameter of a cube that belongs to the APB will be equal to 0.

In order to visualize the interface, we have used 2-dimensional maps. These maps are obtained in the following way. We select a slice  $\Delta z$  along the Z-axis and we average

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<sup>1</sup> Anti-phase boundaries are interfaces leading a phase shift in the scattering amplitudes between two domains. They may be distinguished from those where the two domains differ in orientation.

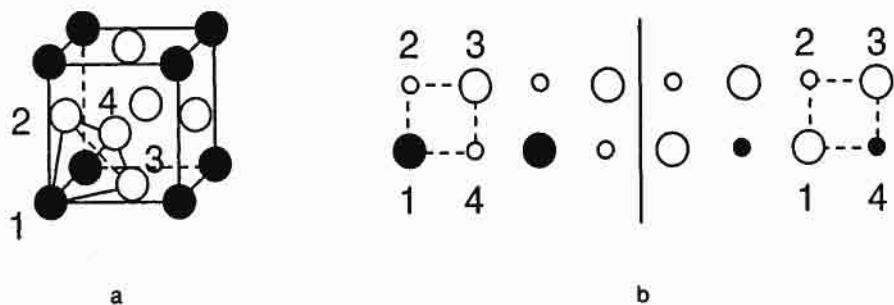


Figure 1: (a) The four cubic sub-lattices and the  $L_{12}$  structure. (b) Non-conservative  $[100]$  APB in the  $L_{12}$  phase. Full (empty) circles represent the minority (majority) atoms.

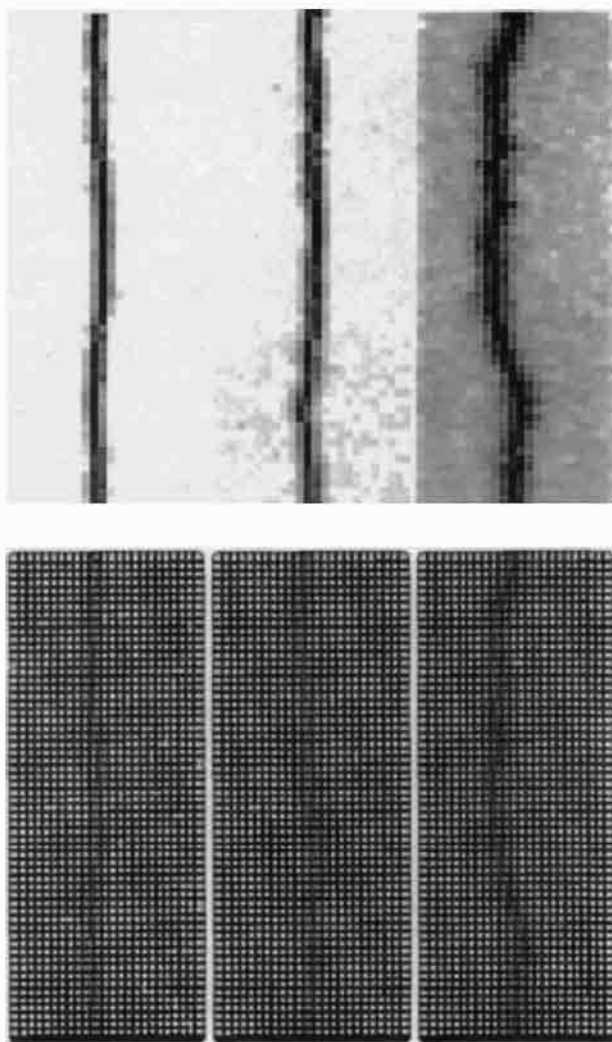


Figure 2: Two-dimensional X-Y order-parameter[upper panel] and spin[lower panel] maps for temperatures 1000 K, 1400 K and 1550 K [lattice sizes  $24 \times 60 \times 60$  in unit of fcc cubes].

any instantaneous local quantities  $[\eta_C(R)$  and  $\sigma_\alpha^C(R)]$  over that range and over some MC sweeps. As example, a 2-dimensional order-parameter map is defined by:

$$\eta(x, y) = \frac{1}{\Delta t \Delta z} \sum_{C \in \Delta t} \int_{z_0}^{z_0 + \Delta z} \eta_C(x, y, z) dz$$

where  $C$  represents a MC configuration at time  $t$  and  $\Delta t$  is the number of configurations (or MC sweeps) over which we define an ensemble average. We define in the same way the 2-dimensional quantities  $\sigma_\alpha(x, y)$ ,  $\alpha=1,2,3,4$ . In the following, we choose  $\Delta z=10$  and  $\Delta t=50$ .

Finally, a 2-dimensional order-parameter map is obtained through the representation of the absolute value of  $\eta(x, y)$  on a grey scale: a perfectly white (black) square represent a perfectly ordered (disordered) fcc cube. These order-parameter maps mimic in some way a dark field image obtained in an electron microscopy study. On the other hand, a plot of the four  $\sigma_\alpha(x, y)$ 's using a grey scale (white corresponding to the minority atom and black to the majority atom) leads to a 2-dimensional spin map which is close to a high resolution image.

## RESULTS

We display in Fig. 2 some 2-d order-parameter and spin maps at different temperatures. These pictures already gives us a qualitative informations on the thermodynamical behavior of the APB. The APB appears to be flat for  $T=1000$  K and  $1400$  K, while it seems to be rough at  $T=1550$  K. It becomes even more rough at higher temperature  $T=1675$  K, as shown in Fig. 3. This visual analysis shows us, without any ambiguity, that the APB does indeed undergo a roughening transition as the temperature increases.

In order to get a quantitative analysis of the roughening transition, we now investigate the order parameter profile of the APB. This profile is defined by averaging the local order parameter  $\eta_C(R)$  over the directions parallel to the APB, *i.e* Y and Z, and over time. Before using this averaging procedure, we must take into account the fact that the APB, if rough, is delocalized. A rough APB is not pinned any more on the lattice sites and moves freely through the lattice. If we do not correct for this movement, the averaging over time would lead to a flat profile. As in ref(4) we then proceed as follows.

For each configuration  $C$ , we average over Y and Z to get an order-parameter profile  $\eta_C(x)$  that depends on  $C$ :

$$\eta_C(x) = 1/L_{\parallel}^2 \sum_{y,z} \eta(x, y, z)$$

We then look for the interface position  $h(C)$  by requiring<sup>4</sup>

$$|\sum_{x=1}^{L_{\perp}} \eta_C(x + h(C) - L_{\perp}/2)| = \min(\approx 0)$$

where the instantaneous profile  $\eta_C(x)$  has been continued periodically. We then proceed to a time average and define the average order parameter profile by:

$$\eta(x) = 1/N_C \sum_C \eta_C(x + h(C) - L_{\perp}/2)$$

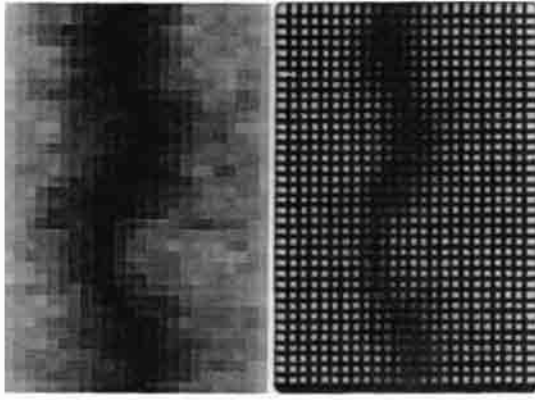


Figure 3: Two-dimensional X-Y order-parameter and spin maps for temperature 1675 K [lattice sizes  $24 \times 36 \times 36$  in unit of fcc cubes].

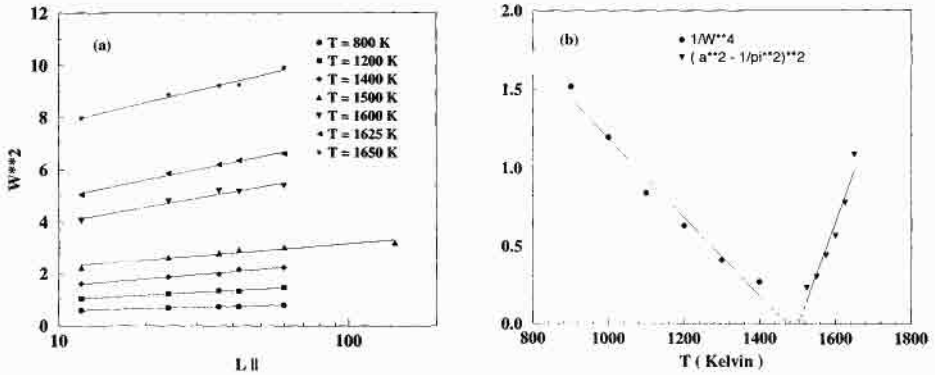


Figure 4: (a) Width  $W^2$  of the antiphase boundary versus  $L_{\parallel}$  for  $24 \times L_{\parallel} \times L_{\parallel}$  lattices at various temperatures. For temperature 1500 K, we have gone up to the transverse size  $L_{\parallel}=144$  while for others it is up to 60. (b)  $1/W^4$  versus  $T$  and  $[a^2 - 1/\pi^2]^2$  versus  $T$  (see text).

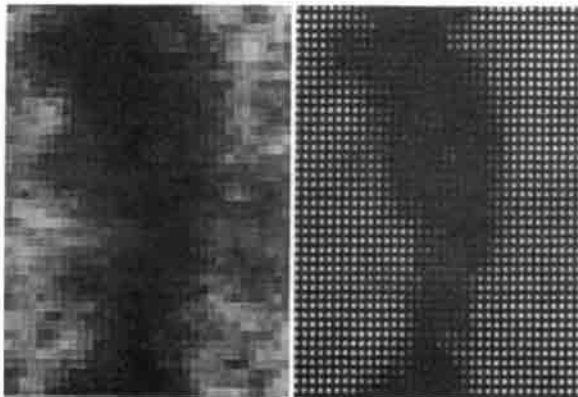


Figure 5: Two-dimensional X-Y order-parameter and spin maps for temperature 1687 K.

where  $N_C$  is the number of the MC configurations that we consider for averaging (we have used the last 10,000 configurations after getting rid of the first few hundreds). We then define the width of this averaged profile through the second moment of the gradient of  $\eta(x)$ :

$$W^2 = \frac{\int x^2 g(x) dx}{\int g(x) dx}$$

where

$$g(x) = \eta(x) - \eta(x - 1)$$

According to the capillary wave approximation<sup>5</sup>, a rough interface is characterized by a width  $W^2$  that diverges logarithmically with its transverse dimensions:

$$W^2 \sim a^2 \ln(L_{\parallel}) \quad (1)$$

The roughening transition<sup>6</sup> itself is believed to be of the Kosterlitz-Thouless type<sup>7</sup>, according to which one should expect the following properties:

$$T < T_R : W^2 \propto (T_R - T)^{-1/2} \quad (2)$$

and

$$T > T_R : a^2 \propto \pi^{-2} + \text{const}(T - T_R)^{1/2} \quad (3)$$

In Fig. 4(a) we show the plot of  $W^2$  as a function of  $L_{\parallel}$ , for different temperatures. At low temperature, the slope is small while it increases significantly at higher temperatures. By fitting  $W^2$  to a logarithmic law, we extract the coefficient  $a^2$  (see Eq.1 and Fig. 4(a)). We show in Fig.4(b) the plot of  $1/W^4$  and of  $(a^2 - 1/\pi^2)$  versus temperature. Our data reproduce satisfactorily the expected linear behavior in  $(T - T_R)$  (see Eq.2 and Eq.3) with  $T_R \sim 1490 \pm 20$  K (we recall that the bulk transition temperature  $T_b$  is  $1690 \pm 2$  K).

The above results show that the APB undergoes a roughening transition at  $T_R \simeq 1490$  K, which is below the bulk first-order transition, and this transition is in agreement with the Kosterlitz-Thouless theory. In brief, the APB is flat below  $T_R$  and, above  $T_R$ , it develops transverse fluctuations and wanders through the lattice.

We know that another interesting phenomenon occurs when the temperature increases up to the bulk transition  $T_b$ . Previous studies<sup>8,9</sup> have shown that the APB is wetted by the disordered phase: a large layer of disordered phase develops in between the two ordered domains. In other words, the APB is splitted into two order-disorder interfaces, whose separation diverges as  $\ln(T_b - T)$ . We display in Fig. 5 the 2-dimensional maps for  $T=1687$  K, *i.e.* very close to the first-order transition. As expected, we see that the APB separates into two order-disorder interfaces. Moreover, the width of the penetrating disordered layer varies along the APB. This means that each order-disorder interface develops its own transverse fluctuations and that the APB begins to behave as two separate objects.

## CONCLUSIONS

In summary, we have presented here a detailed MC investigation of an interface in a situation where the bulk disordering transition is of first order. Using two-dimensional

order-parameter and spin maps, we have shown that the APB undergoes a roughening transition at a temperature  $T_R$  which is definitely below the bulk disordering temperature. A quantitative analysis shows that this roughening transition is of Kosterlitz-Thouless type. Finally, a preliminary study close to bulk transition indicates that the APB separates into two order-disorder interfaces that develop their own fluctuations.

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# EFFECTIVE PAIR INTERACTIONS IN RANDOM ALLOYS BY DIRECT CONFIGURATIONAL AVERAGING

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## 1. Introduction

We have recently succeeded in calculating the defect energies in metals, such as I-I (I=impurity), P-I (P=probe), V-I (V=vacancy) interaction energies (IE's).<sup>1</sup> The calculations apply the Korringa-Kohn-Rostoker (KKR) Green's function method for impurities and are based on the local-spin-density approximation (LSDA) for density-functional theory. The nice agreement of calculated results for P-I IE's with available accurate measured values<sup>2</sup> seems to demonstrate the accuracy of our calculations. It was also shown that the Monte Carlo simulations based on the calculated I-I IE's reproduce very well the measured values of temperature-concentration dependence for the solid solubility limit of impurities in metals.

The aim of the present paper is to apply the impurity KKR Green's function method to the study of nearest-neighbor effective-pair interaction energies (NN-EPIE's) in low-concentrated *fcc* disordered alloys  $H_{1-c}X_c$  ( $H$  = host,  $X$  = impurity;  $c \leq 0.1$ ). It is easily expected that if the impurity-cluster size is large and the various atomic configurations in the clusters are taken into account, the present method will give accurate estimation for EPIE's. The present work takes into account the alloy effect (*randomness*) by the direct configurational averaging (DCA) method, being used recently by deFontaine's group,<sup>3</sup> which treats accurately the multi-site effect. In the present calculations we use the smallest impurity cluster including only up to the nearest-neighboring atoms (3-20) around the impurity pair (1-2), shown in Fig.1. In Sec.2 we discuss the accuracy of this nearest-neighbor approximation. Sec.3 gives the calculated results for  $Cu_{1-c}Ni_c(Ni_{1-c}Cu_c)$ ,  $Pd_{1-c}V_c$ ,  $Ni_{1-c}Al_c(Al_{1-c}Ni_c)$ . We show results of *dilute limit* ( $c=0.1$ ) and low concentrations ( $c=1/18, 2/18$ ). It is shown from the comparisons with the experimental results and the calculated results of KKR-CPA-GPM that the charge transfer effect is important for  $Pd_{1-c}V_c$ . Summary is given in Sec.4.

## 2. Method

The practicality and accuracy of the present method depend on the following two factors (1) the impurity-cluster size and (2) the number of atomic configurations used



in the DCA.<sup>3</sup>

### 2.1 Impurity-cluster size; nearest-neighbor approximation

Figure 2 shows the calculated results for the IE's of impurity dimers (X-X) in *Cu* and *Ni* (*CuCu*<sub>18</sub>X<sub>2</sub> and *NiNi*<sub>18</sub>X<sub>2</sub>); the potentials in the impurity cluster are determined self-consistently.<sup>1</sup> In order to clarify the accuracy of nearest-neighbor approximation, we also calculated the IE's of impurity dimers where the nearest-neighboring atoms are of Ni element, but all atoms outside the impurity cluster are of Cu element (*CuNi*<sub>18</sub>X<sub>2</sub>). It is seen that the calculated results for *NiNi*<sub>18</sub>X<sub>2</sub> are very close to those of *CuNi*<sub>18</sub>X<sub>2</sub>. This means that the IE's of impurity dimer are determined mainly by the environment of nearest-neighbor shell. It is easily expected that the lower the concentration, the better the nearest-neighbor approximation. Thus, we believe that the present calculations for EPIE's, based on the nearest-neighbor approximation are reliable, at least, for low-concentrated alloys of similar elements if the *randomness* is treated accurately.

### 2.2 Number of atomic configurations used in the DCA

The NN-EPIE's in the disordered alloy *H*<sub>1-*c*</sub>X<sub>*c*</sub>, *E*<sub>int</sub><sup>alloy</sup>, are defined as the total-energy difference between two states, as shown in Fig.3: (1) the final one where the two X impurities are located at nearest-neighbor sites 1 and 2 in *H*<sub>1-*c*</sub>X<sub>*c*</sub> (Fig.1) and (2) the initial one where both atoms are infinitely apart in *H*<sub>1-*c*</sub>X<sub>*c*</sub>. Substituting *c*X + (1 - *c*) H for the averaged atoms at the center (1,2 in Fig.1) in the cluster, we can obtain *E*<sub>ite</sub><sup>alloy</sup> = (1 - *c*)<sup>2</sup>(*E*<sub>XX</sub><sup>alloy</sup> + *E*<sub>HH</sub><sup>alloy</sup> - 2*E*<sub>XH</sub><sup>alloy</sup>); it is noted that the factor (1 - *c*)<sup>2</sup> will be important to discuss the concentration dependence of Pd<sub>1-*c*</sub>V<sub>*c*</sub>, as discussed in

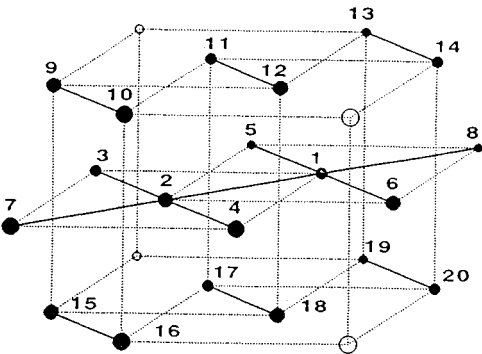


Fig.1 The 20-atom cluster used in the present calculations. All the atoms are on fcc sites; two impurity sites (1,2) and the neighboring sites (3-20).

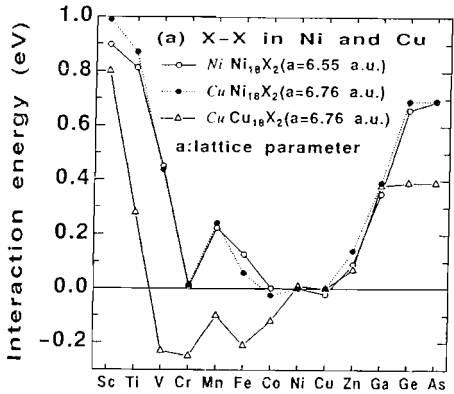


Fig.2 Interaction energies of impurity dimers (X-X) in Ni and Cu as well as those for the impurity dimers where the nearest-neighboring atoms are of Ni element, but all the atoms outside are of Cu element.

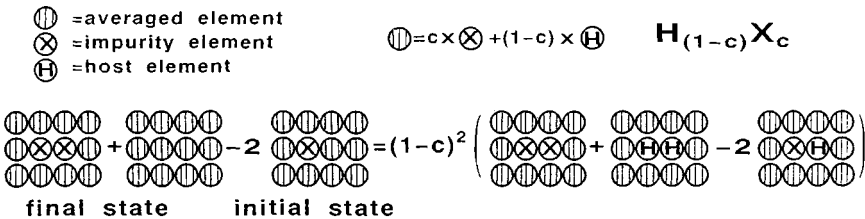


Fig.3 Schematic representation of initial and final states to calculate effective pair (X-X) in interaction energies in a disordered alloy *H*<sub>1-*c*</sub>X<sub>*c*</sub>.

Sec.3.2. Thus we need the calculations for three kinds of pairs in  $H_{1-c}X_c$ ; XX, HH, and XH. The alloy effect of the nearest-neighboring atoms (3-20 in Fig.1) are treated by the DCA. For  $c=1/18$ , there are 18 ( $=_{18}C_1$ ) configurations since one X occupies one of 18 sites (3-20). From a consideration of symmetry around impurity pairs, they are divided into 7 kind of groups, (3,4), (5,6), (7), (8), (9,10,15,16), (11,12,17,18), (13,14,19,20). Thus, for  $c=1/18$  we can easily perform the exact averaging by taking into account only 7 inequivalent configurations. However, for higher concentrations we will use a small number, say 10, of atomic configurations generated by Monte Carlo method since a number of configurations increases rapidly with the concentration; for  $c=2/18$ , there are 153 ( $=_{18}C_2$ ) which divides into 54 inequivalent configurations. The accuracy of averaging over the small number of configurations was discussed by deFontaine's group.<sup>3</sup>

### 3. Calculated results

We discuss the results of IE's of *dilute limit* in 3.1 and the results of EPIE's of low concentrations in 3.2.

Table I. Pair interaction energies (in eV) of 1-4th neighbors in Alloys. The values of *dilute limit* are shown.

| Alloys | 1st   | 2nd   | 3rd   | 4th   |
|--------|-------|-------|-------|-------|
| CuNi   | 0.01  | 0.01  | 0.01  | 0.06  |
| NiCu   | -0.02 | 0.00  | 0.00  | -0.01 |
| AgPd   | 0.04  | 0.00  | 0.00  | 0.00  |
| PdAg   | 0.00  | 0.00  | 0.01  | -0.01 |
| PdV    | 0.48  | 0.07  | 0.06  | 0.12  |
| NiV    | 0.45  | -0.15 | -0.02 | 0.04  |
| NiAl   | 0.39  | 0.00  | 0.00  | -0.02 |
| AlNi   | 0.16  | 0.03  | 0.01  | -0.00 |

#### 3.1 *dilute limit*

Table I shows the calculated results of *dilute limit*. It is obvious that the nearest-neighbor interactions are of major importance. The fundamental characteristic features of ordering systems such as PdV, NiV, and NiAl are explained by the large positive value of the NN IE's; positive means repulsion between the two impurity atoms. The continuous solid solubilities of CuNi and AgPd correspond to the small values of the IE's.<sup>1</sup>

#### 3.2 low concentration ( $c=1/18, 2/18$ )

Figure 4 shows the calculated results for CuNi, PdV, NiAl. The concentration-dependence of EPIE's for CuNi is very small, as expected by the results of a *dilute limit* (Cu-rich end and Ni-rich end).

For PdV, we can find that the EPIE's decrease with the concentration of V. This may be explained by considering the reduction of an increased number of strong NN V-V bonds, caused by the atomic rearrangement due to the formation of impurity V dimer; a number of V-V bond increases by 1 for *dilute limit* ( $c=0$ ), while its increase is reduced by a factor  $(1-c)^2$  for  $Pd_{1-c}V_c$ . If we use the value of V-V NN IE of *dilute limit*, the decrease is 0.48  $(1 - (1-c)^2)$ ; for  $c=1/18$  it is  $\sim 0.05$  eV which reproduce almost half of the value ( $\sim 0.1$ ) obtained by the present calculations. This simple explanation for the decrease of NN EPIE's around low-concentration may also be useful for TM-TM (TM=transition metal) alloys of strong short-range repulsive interactions, such as  $Ni_{1-c}V_c$ . It is seen in Fig.4 that the present EPIE's are shifted upward by  $\sim 0.07$  eV, compared with the KKR-CPA-GPM results<sup>4</sup> shown in Fig.4; it is noted that the KKR-CPA-GPM results include only the band-energy changes. In order to examine the discrepancy between two calculations, we calculated EPIE's by use of frozen-potential approximation (FPA) which also treats only the band-energy changes. The EPIE's obtained by FPA are fairly small compared with the self-consistent results, as seen in Fig.4: for a FP of V we use the potential of an isolated impurity V in Pd. It is found that the FPA overestimates the intercell *electrostatic energy* (negative) due to the charge transfer since the charge transfer is overestimated by the non-self-consistent

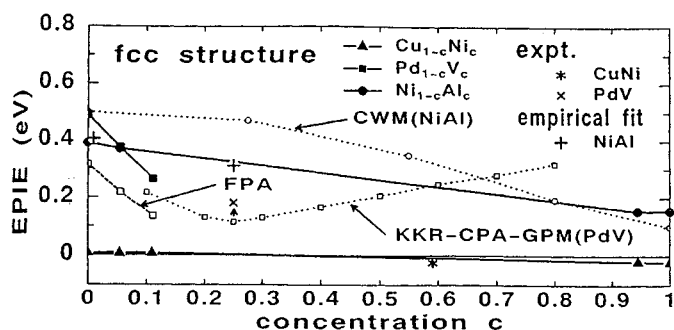


Fig.4 Effective pair interaction energies of CuNi, PdV, NiAl as well as the experimental values.<sup>6,8</sup> The KKR-CPA-GPM result for PdV and the CWM result for NiAl are also shown for comparison.

calculations.<sup>5</sup> Presumably this is the case for the KKR-CPA-GPM calculations. Thus we may expect that the present calculations reproduce the experimental result ( $\sim 0.18$  eV for  $\text{Pd}_{0.75}\text{V}_{0.25}$ ), obtained via the Inverse Monte Carlo method from the diffuse scattering studies,<sup>6</sup> since the discrepancy ( $\sim 0.07$  eV) of the KKR-CPA-GPM result (0.11 eV) with the experimental result (0.18 eV) may be corrected by the present accurate treatment of the charge transfer.

Lastly we discuss the EPIE's of NiAl. The decrease around Ni-end may be explained as mentioned above since the NN Al-Al IE is strongly repulsive; the decrease is 0.04 eV for  $c=1/18$  by the simple model, while 0.02 eV by the present calculations. It is also seen in Fig. 4 that the present results qualitatively agree with the results obtained by the Connolly-Williams method (CWM);<sup>7</sup> it is not necessary to get the quantitative agreements since the CWM doesn't give unique EPIE's. However, it should be noted that the present calculations agree with the EPIE's obtained from a fit to the Ni-rich part of Ni-Al phase diagram based on empirical Lennard-Jones potentials.<sup>8</sup>

#### 4. Summary

It is shown that the impurity KKR-Green's function method combined with a DCA technique is powerful to investigate the EPIE's of, at least, low-concentrated disordered alloys. The agreement with the experimental results seem to be nice. For  $\text{Pd}_{1-c}\text{V}_c$  we showed that the charge transfer is important and that the concentration dependence of EPIE's may be explained by the reduction of an increased number of strong V-V bonds, caused by the rearrangement due to the formation of impurity V-V bond.

However, for high-concentrated alloys it becomes important to treat the alloy effects outside the impurity cluster. The use of CPA medium is strongly suggested.

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## THEORY OF SURFACE SEGREGATION: SELF-CONSISTENT DETERMINATION OF THE CONCENTRATION PROFILE

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### INTRODUCTION

Ab-initio studies of surface segregation in alloys are based on the Ising-type Hamiltonian, whose parameters are the effective cluster interactions (ECI). The ECIs for alloy surfaces can be determined by various methods, e.g., by the Connolly-Williams inversion scheme<sup>1-3</sup>, or by the generalized perturbation method (GPM)<sup>4</sup>. The GPM relies on the force theorem<sup>5</sup>, according to which only the band term is mapped onto the Ising Hamiltonian in the bulk case. The case of macroscopically inhomogeneous systems, like disordered surfaces is more complex. The ECIs can be determined on two levels of sophistication:

(i) The single-site charge densities, the atomic potentials and the CPA effective reference medium are those of the homogeneous bulk alloy, and the redistribution of the electronic charge in the surface region and accompanying electrostatic fields are neglected. The ECIs are determined by mapping only the band term onto the Ising Hamiltonian, as the core, double-counting, Madelung and non-spherical terms do not contribute. This approach (hereafter referred to as model I) was used in previous papers<sup>6-9</sup>.

(ii) The single-site charge densities, atomic potentials, and the CPA effective medium are determined in a fully selfconsistent calculation of the surface electronic structure including the redistribution of charge in the surface region. It then follows from the force theorem that even if the local environment effects are neglected, it is necessary to include besides the band term also contributions from all other terms (core, double-counting, Madelung and non-spherical). A great advantage of this formulation (referred to as model II) follows from the fact that it allows for a selfconsistent determination of the concentration profile. In the first step, the surface electronic structure is cal-

culated from first principles for an arbitrary inhomogeneous concentration profile and the corresponding ECIs are determined. In the next step, a new concentration profile is found from the ECIs using the methods of statistical mechanics. These two steps are repeated until a consistency between the electronic structure and the concentration profile is achieved. The method for calculating the Ising Hamiltonian parameters for an arbitrary concentration profile was developed very recently<sup>10,11</sup>, so we summarize only the most important formulas, and concentrate on a selfconsistent determination of the concentration profile in the surface region of segregating alloys.

## THEORY

The electronic structure is calculated by the all-electron relativistic version<sup>12</sup> of the TB-LMTO-CPA method within the atomic sphere approximation (ASA), but taking into account the charge redistribution between different layers and the deviations of the atomic charge densities in the surface region from spherical symmetry by including the net charges and dipole moments<sup>13-15</sup>. The electrostatic potential barrier across the solid-vacuum interface (and the closely related work function) as well as the surface energy sensitively depend on the details of the charge distribution as given by the layer dependence of the atomic net charges and the non-spherical character of the charge distribution inside the atomic spheres.

A particular configuration  $\Gamma$  of a semi-infinite disordered binary alloy  $A_xB_{1-x}$  is characterized by a set of occupation indices  $\{\eta_{\mathbf{R}}^Q\}$ , where  $\eta_{\mathbf{R}}^Q = 1$  if the site  $\mathbf{R}$  is occupied by an atom of the type  $Q$ , and  $\eta_{\mathbf{R}}^Q = 0$  otherwise. Configurational averaging of occupation indices  $\langle \eta_{\mathbf{R}}^Q \rangle = c_{\mathbf{R}}^Q$  yields the local concentrations  $c_{\mathbf{R}}^Q$ . The energy of such a configuration can be expressed in the form of an effective Hamiltonian of Ising type

$$H_I = E_0 + \sum_{\mathbf{R}Q} D_{\mathbf{R}}^Q \eta_{\mathbf{R}}^Q + \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'Q'Q''} V_{\mathbf{R}\mathbf{R}'}^{QQ'} \eta_{\mathbf{R}}^Q \eta_{\mathbf{R}'}^{Q'} + \dots \quad (1)$$

The parameters of the semi-infinite alloy Ising Hamiltonian are the configurationally independent part of the alloy internal energy  $E_0$ , the on-site energies  $D_{\mathbf{R}}^Q$ , the interatomic pair interactions  $V_{\mathbf{R}\mathbf{R}'}^{QQ'}$ , and generally, interatomic interactions of higher order. For simplicity we limit ourselves to the on-site terms and pair interactions only, although triplets, quadruplets, etc., can be studied along the same lines.

Most of the present implementations of the CPA on the ab-initio level, both for bulk and surface cases, assume a lattice occupied by atoms with equal radii of Wigner-Seitz (or muffin-tin) spheres. The effect of charge transfer which can seriously influence the alloy energetics<sup>16</sup> is often neglected. Several methods were proposed to account for charge transfer effects in bulk alloys, e.g., the so-called correlated CPA<sup>17</sup>, or the screened-impurity model<sup>18</sup>. The application of these methods to alloy surfaces seems to be rather complicated.

A different approach is adopted here. Within the LMTO-ASA method, it is possible to vary the atomic radii in such a way that the net charges  $q_{\mathbf{R}}^{(00)}$  are non-random while preserving the total volume of the system<sup>19,20</sup>. The basic assumption of a single-site theory of electronic structure of disordered alloys, namely that the potential at any site  $\mathbf{R}$  depends only on the occupation of this site by atom  $A$  or  $B$ , and is completely independent of the occupation of other sites, is fulfilled, if the net charges  $q_{\mathbf{R}}^{(00)}$ , and the multipoles  $q_{\mathbf{R}}^L$  ( $L = (\ell, m), \ell > 0$ ), are non-random and independent of the occupation of the lattice sites by atoms  $A$  or  $B$ . The dipole moments for atoms  $A$  and  $B$  are not identical, but the differences  $q_{\mathbf{R}}^{L,A} - q_{\mathbf{R}}^{L,B}$  are rather small. The randomness of

multipoles  $q_{\mathbf{R}}^L$  is neglected in the construction of atomic potentials, while the differences  $q_{\mathbf{R}}^{L,A} - q_{\mathbf{R}}^{L,B}$  are included in the expression for total energy and in the Ising Hamiltonian parameters.

In the bulk case, the atomic sphere radii  $s^Q$  are adjusted such that each atomic sphere is charge neutral. The Madelung contribution to the effective potential and the Madelung contribution to the total energy then vanish. The absence of these Madelung contributions is compensated by a change in the potential parameters which follows from modified sphere radii  $s^Q$ . In the surface case, the situation is more difficult as the spheres cannot be neutral because of the charge redistribution at the solid-vacuum interface. However, by adjusting the sphere radii it is possible to achieve that the net charges on A and B atoms in the same layer are equal, i.e., non-random. The non-zero net charges and dipoles in the surface region then give rise to a non-random electrostatic field. It should be noted, however, that using spheres with different radii can bring serious problems connected with uneven overlaps between the spheres. The larger the mismatch of the sphere radii, the larger will be the error in determining the electronic structure. A possible remedy is the formalism of Blackman, Esterling and Berk, which was already successfully applied to disordered bulk alloys<sup>21</sup>, but can be extended also to their surfaces.

The on-site energy  $D_{\mathbf{R}}^Q$  for atomic species  $Q$  at the lattice site  $\mathbf{R}$  consists of the band, core, double-counting, non-spherical and Madelung contributions, respectively,

$$\begin{aligned} D_{\mathbf{R}}^Q = & -\frac{1}{\pi} \text{Im} \int_{-\infty}^{E_F} dE \text{tr} \ln \left[ 1 - \left( P_{\mathbf{R}}^Q(z) - \mathcal{P}_{\mathbf{R}}(z) \right) \bar{g}_{\mathbf{R}\mathbf{R}}(z) \right] \\ & + \sum_j^{\text{core}} \left( \varepsilon_{\mathbf{R}j}^Q - \varepsilon_{\text{bulk},j}^Q \right) + \left( \Phi_{dc}[\rho_{\mathbf{R}}^Q] - \Phi_{dc}[\rho_{\text{bulk}}^Q] \right) \\ & + \left( \Phi_{ns}[\rho_{\mathbf{R}}^Q] - \Phi_{ns}[\rho_{\text{bulk}}^Q] \right) + \left\{ -2Z^Q \phi_{\mathbf{R}}^{(00)} + \sum_{L(\ell>0)} q_{\mathbf{R}}^{L,Q} \phi_{\mathbf{R}}^L \right\}, \end{aligned} \quad (2)$$

where  $z = E + i0$ ,  $E_F$  is the average (CPA) Fermi energy,  $P_{\mathbf{R}}^Q(z)$  is the potential function,  $\mathcal{P}_{\mathbf{R}}(z)$  is the coherent potential function, and  $\bar{g}_{\mathbf{R}\mathbf{R}}(z)$  is the on-site block of the configurationally averaged auxiliary Green's function<sup>19</sup>. The core, double counting and non-spherical contributions of atoms from the bulk region are subtracted from the  $D_{\mathbf{R}}^Q$ . The on-site terms then express the net difference between the surface and bulk atoms. The core states are calculated selfconsistently in order to describe correctly their reaction to the changes of atomic potentials in the surface region and to include the changes in the normalization caused by varying radii of adjustable atomic spheres. The functionals  $\Phi_{dc}$  and  $\Phi_{ns}$  represent the on-site double-counting and non-spherical energy<sup>11</sup>, respectively. The Madelung potential  $\phi_{\mathbf{R}}^L$  acting onto a multipole  $q_{\mathbf{R}}^L$

$$\phi_{\mathbf{R}}^L = 2 \sum_{\mathbf{R}'(\mathbf{R}' \neq \mathbf{R})} \sum_{L'} \mathcal{M}_{\mathbf{R}\mathbf{R}'}^{LL'} \langle q_{\mathbf{R}'}^{L'} \rangle, \quad (3)$$

is defined via the multipole-multipole interaction constants  $\mathcal{M}_{\mathbf{R}\mathbf{R}'}^{LL'}$ . The pair interactions are given by

$$\begin{aligned} V_{\mathbf{R}\mathbf{R}'} &= V_{\mathbf{R}\mathbf{R}'}^{AA} + V_{\mathbf{R}\mathbf{R}'}^{BB} - V_{\mathbf{R}\mathbf{R}'}^{AB} - V_{\mathbf{R}\mathbf{R}'}^{BA} \\ &= -\frac{1}{\pi} \text{Im} \int_{-\infty}^{E_F} dE \text{tr} \ln \left[ 1 - \tau_{\mathbf{R}}(z) \bar{g}_{\mathbf{R}\mathbf{R}'}(z) \tau_{\mathbf{R}'}(z) \bar{g}_{\mathbf{R}'\mathbf{R}}(z) \right] \\ &\quad + \sum_{L(\ell>0)} \sum_{L'(\ell'>0)} (q_{\mathbf{R}}^{L,A} - q_{\mathbf{R}}^{L,B}) \mathcal{M}_{\mathbf{R}\mathbf{R}'}^{LL'} (q_{\mathbf{R}'}^{L',A} - q_{\mathbf{R}'}^{L',B}), \end{aligned} \quad (4)$$

where  $\tau_{\mathbf{R}}$  is the difference of  $t$ -matrices for  $A$  and  $B$  atoms,  $\tau_{\mathbf{R}}(z) = t_{\mathbf{R}}^A(z) - t_{\mathbf{R}}^B(z)$ . The first term in (4) is the band energy contribution, as given by the GPM. The second term represents electrostatic interactions of higher multipoles and is usually negligibly small.

Once the effective Ising model has been defined, thermodynamic properties like the equilibrium composition of the surface layers can be studied using the Monte Carlo simulation technique<sup>8</sup>. In the present Monte Carlo study, a three dimensional fcc rigid lattice is represented by a finite number of atoms (typically 2000 atoms). To minimize boundary effects, the alloy is assumed to be periodic in the two directions parallel to the surface. For the fcc (001) surface we have used eight layers each containing  $N_p = 15 \times 17$  atoms. The top layer is the simulated surface. The bottom plane and the plane just above it are regularly supplied with atoms corresponding to the average bulk composition. Each simulation involves several million of basic Monte Carlo steps resulting thus in a set of atomic configurations corresponding to the thermal equilibrium. The desired quantities such as the concentration profile are then obtained by averaging over the resulting configurations<sup>8</sup>.

## RESULTS AND DISCUSSION

We have applied the method described above to study the surface segregation of the Cu-Ni alloys in a broad range of concentrations<sup>11</sup>. Here we present the results for the (001) surface of the fcc  $\text{Ag}_{25}\text{Pd}_{75}$  alloy. The experimental bulk alloy phase diagram of Ag-Pd displays a continuous set of solid solutions over the whole range of concentrations for temperatures above 1100 K; at lower temperatures, there are controversial data indicating either the miscibility gap, or the formation of compounds. The surface segregation in Ag-Pd alloys was studied both experimentally<sup>22</sup> and theoretically<sup>23</sup> and it is agreed that Ag segregates to the surface. All Monte Carlo simulations were performed at 800 K. The selfconsistent calculations of the segregation profile were started from the homogeneous profile corresponding to the bulk composition. In order to test the dependence of the final result on the initial condition, we performed also the other set of calculations starting from the concentration profile predicted by the non-selfconsistent theory (model I). Both these calculations lead after 4 iterations to the identical profile, and two iterations more were needed to achieve selfconsistency, with an accuracy of order 0.5 % between the previous and new concentration profile. The results are summarized in Tables 1-3 below.

The first point to emphasize is that the bulk values of the pair interactions lead to the occurrence of a miscibility gap in the bulk system. We are in a complete agreement with Ouannasser et al.<sup>23</sup>, but in contradiction with ASW-based calculations<sup>24</sup> which give an ordering system. The second point concerns the concentration profile. The non-selfconsistent theory (model I) yields already qualitatively correct values  $\Delta^I$  for the on-site terms corresponding to the segregation of silver atoms at the surface. The selfconsistent theory (model II) leads to a reduction of the on-site terms in comparison with the model I. In the selfconsistent theory, the on-site terms result from a delicate interplay between the band, core, double-counting and Madelung contributions. Some of these contributions are rather large, but they mostly cancel each other.

According to Table 3, the pair interactions converge to their bulk values, but the differences between their surface and bulk values are quite pronounced, larger than in the non-selfconsistent theory. In the model I, the surface value of the first nearest neighbor pair interaction is -0.34 mRy, to be compared with 6.28 mRy found for model

II. The change of the sign between these two models may be also important for clustering and the surface growth mechanism. In the selfconsistent theory, the silver atoms tend to establish bonds with palladium atoms, while in the non-selfconsistent theory, the Ag-Ag bonds are favored. This explains the differences between the concentration profiles calculated within the models I and II and the fact that they do not simply follow the variations of the on-site terms.

**Table 1.** Segregation profiles at the (001) surface of fcc Ag<sub>25</sub>Pd<sub>75</sub> alloy calculated for models I and II, and as given by Ounasser et al.<sup>23</sup>.

|                 | concentration of Ag atoms in layer |       |       |       |      |
|-----------------|------------------------------------|-------|-------|-------|------|
|                 | 1                                  | 2     | 3     | 4     | bulk |
| model I         | 0.99                               | 0.60  | 0.18  | 0.26  | 0.25 |
| model II        | 1.00                               | 0.985 | 0.216 | 0.176 | 0.25 |
| Ounasser et al. | 0.86                               | 0.40  | 0.27  | 0.25  | 0.25 |

**Table 2.** Difference of the on-site terms  $\Delta = D^A - D^B$  (in mRy) of the effective Ising Hamiltonian for a (001) surface of fcc Ag<sub>25</sub>Pd<sub>75</sub> as calculated within model II for the converged inhomogeneous concentration profile. Individual contributions from the band energy, core electrons, double-counting terms, Madelung energy and non-spherical corrections, both electrostatic (nse) and exchange-correlation (nsxc) are given. Their sum,  $\Delta^{II}$ , is compared with the result of model I,  $\Delta^I$ .

| layer | $\Delta^{band}$ | $\Delta^{core}$ | $\Delta^{dct}$ | $\Delta^{Mad}$ | $\Delta^{nse}$ | $\Delta^{nsxc}$ | $\Delta^{II}$ | $\Delta^I$ |
|-------|-----------------|-----------------|----------------|----------------|----------------|-----------------|---------------|------------|
| 1     | -550.92         | -2808.75        | 3484.35        | -148.59        | -0.51          | 0.07            | -24.35        | -39.46     |
| 2     | -287.75         | -1509.73        | 1759.27        | 47.65          | 0.18           | 0.02            | 9.63          | -5.64      |
| 3     | -85.26          | -550.49         | 637.54         | 3.07           | 0.07           | 0.02            | 4.95          | -2.71      |
| 4     | 50.60           | 108.64          | -157.08        | 0.95           | 0.00           | 0.00            | 3.10          | -2.03      |

**Table 3.** Renormalized pair interactions (in mRy) for the (001) surface of fcc Ag<sub>25</sub>Pd<sub>75</sub> alloy for the converged inhomogeneous concentration profile.

| neighbor | layers |      |       |       |      |       |       |       |       |       |
|----------|--------|------|-------|-------|------|-------|-------|-------|-------|-------|
|          | 1-1    | 1-2  | 1-3   | 2-2   | 2-3  | 2-4   | 3-3   | 3-4   | 4-4   | bulk  |
| 1        | 6.28   | 3.79 | -     | 0.93  | 0.80 | -     | -0.73 | -0.37 | -1.74 | -0.92 |
| 2        | 0.46   | -    | 1.39  | 1.20  | -    | 1.14  | 0.42  | -     | 0.65  | 0.12  |
| 3        | -      | 0.38 | 0.72  | -     | 0.25 | 0.25  | -     | 0.14  | -     | 0.18  |
| 4        | 0.13   | -    | -0.23 | -0.12 | -    | -0.13 | -0.58 | -     | -0.45 | -0.46 |

## CONCLUSIONS

We have developed a theory that allows to determine the effective cluster interactions for surfaces of disordered alloys. It is based on the selfconsistent electronic structure of surfaces and includes the charge redistribution at the metal/vacuum interface. It can yield effective cluster interactions for any concentration profile and permits to determine the surface concentration profile from first principles in a selfconsistent manner, by



combining a calculation of concentration-dependent Ising parameters for an arbitrary concentration profile with a statistical study providing an updated profile. In this way, a complete and reliable determination of a surface segregation profile can be achieved on an ab-initio level.

## Acknowledgements

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# CALCULATION OF THE ELECTRONIC STRUCTURE OF ANTIFERROMAGNETIC CHROMIUM WITH A SINUSOIDAL SPIN DENSITY WAVE BY THE METHOD OF DIRAC FUNCTION LINEAR COMBINATION

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## Introduction

It has been found experimentally that, at temperatures below 312K, chromium has antiferromagnetic order with a spin density wave (SDW) incommensurate with the lattice constant. The wave vector  $\mathbf{Q} = 2\pi/a * (1 - \delta, 0, 0)$  ( $a$  is the lattice constant and  $\delta \approx 0.05$ ) of the SDW is oriented in the direction of one of the cubic axes. As a consequence the unit cell contains about 40 chemically equivalent atoms with different magnitude of the magnetic moment. The local magnetic moments are collinear and sinusoidally modulated with a maximum value  $M = 0.59\mu_B$ . At a temperature of 118K, the SDW polarization changes from longitudinal to transversal (the spin-flip phase transition).

It is clear that an *ab initio* calculation of the ground state of AF Cr, based on actual experimental data on the magnetic structure, would be at the moment absolutely unfeasible. That is why most calculations are performed for a vector  $\mathbf{Q} = 2\pi/a * (1, 0, 0)$ . In this case Cr has a *CsCl* unit cell. The local magnetic moments at different atoms are equal in magnitude but opposite in direction. Such an approach is used, in particular, in papers [2, 3, 4], in which the electronic structure of Cr is calculated within the framework of spin density functional theory. Our paper [6] is devoted to the study of the influence of relativistic effects on the electronic structure of chromium. The results of calculations demonstrate that the relativistic effects completely change the structure of the Cr electron spectrum, which leads to its anisotropy for the directions being identical in the non-relativistic approach.

In the present paper we suggest a simple technique for calculating the electronic structure in the presence of a SDW, based on the variational Ritz procedure.

## 1 General formalism

In accordance with [11], the Dirac equation for a system with SDW can be written as

$$(\hat{H}_0 + \Delta V \hat{\Sigma})\Psi = \varepsilon \Psi, \quad (1)$$

where  $\Psi$  is a four-component spinor,  $\hat{H}_0$  is the standard Dirac operator

$$\hat{H}_0 = c\hat{\alpha}\hat{\mathbf{p}} + mc^2\hat{\beta} + V\hat{I}. \quad (2)$$

Here

$$\hat{\alpha} = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix} \quad \hat{\beta} = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \quad \hat{\Sigma} = \begin{pmatrix} \sigma_x & 0 \\ 0 & \sigma_x \end{pmatrix} \quad (3)$$

and  $\sigma = (\sigma_x, \sigma_y, \sigma_z)$  are the Pauli matrices,  $I$  is the unit matrix. We also assume the magnetic moment to be oriented in the  $Z$ -direction.

Thus, the effective electron potential at site  $\mathbf{R}_j$  consists of two terms: site-independent average potential  $V(\mathbf{r})$  and an addition connected with spin polarization,  $\Delta V_j(\mathbf{r})$ .

The variational Ritz procedure reduces the problem of solving (1) to solving the generalized eigenvalue problem:

$$\sum_i (H_{ij} - EO_{ij})b_j = 0, \quad j = 1, 2, \dots, N, \quad (4)$$

where  $N$  is the number of basis functions  $\varphi_i(\mathbf{r})$ ;

$$H_{ij} = \int \varphi_i^+(\mathbf{r}) \hat{H} \varphi_j(\mathbf{r}) d\mathbf{r} \quad (5)$$

$$O_{ij} = \int \varphi_i^+(\mathbf{r}) \varphi_j(\mathbf{r}) d\mathbf{r} \quad (6)$$

$\hat{H}$  — is the system Hamiltonian, and  $b_j$  are variational parameters.

The functions  $E(\mathbf{k})$  are determined by the zeros of the secular determinant

$$\det | H_{ij} - EO_{ij} | = 0 \quad (7)$$

The principal distinction between various computational techniques reduces eventually to the choice of basis functions  $\varphi_i(\mathbf{r})$ .

In this paper, for functions  $\varphi_i(\mathbf{r})$  we shall use the four-component spinors  $\psi_i(\mathbf{q}, \mathbf{r})$  being solutions of the Dirac equation

$$\hat{H}_0 \psi_i(\mathbf{q}, \mathbf{r}) = E_i^0 \psi_i(\mathbf{q}, \mathbf{r}) \quad (8)$$

Here  $\mathbf{r}$  varies within the boundaries of a magnetic (extended) cell, and  $\mathbf{q}$  is a wave vector from the corresponding Brillouin zone.

The potential  $V(\mathbf{r})$  in (2) being identical for all atoms in the extended cell, the problem of finding the energy eigenfunctions and eigenvalues in (8) may be reduced to their calculation for a one-atom cell.

The basis functions constructed in this manner automatically satisfy the necessary boundary conditions for a magnetic cell. They are orthonormal in virtue of being eigenfunctions of the Hermitian operator  $\hat{H}_0$ , therefore the overlapping integrals(6) take on the form

$$\int \psi_i^+(\mathbf{q}, \mathbf{r}) \psi_j(\mathbf{q}, \mathbf{r}) d\mathbf{r} = \delta_{ij} \quad (9)$$

The solutions  $\Psi(\mathbf{q}, \mathbf{r})$  of the Dirac equation (1) for the SDW are represented as a linear combination of  $\psi_i(\mathbf{q}, \mathbf{r})$  with variational parameters  $a_i$

$$\Psi(\mathbf{q}, \mathbf{r}) = \sum_i b_i \psi_i(\mathbf{q}, \mathbf{r}) \quad (10)$$

Since it is the  $d$ -electrons that are responsible for the formation of antiferromagnetic order in  $Cr$ , it would be reasonable to take into account in expression (10) only the energy bands with addition of  $3d$ -electrons. In view of double degeneracy, the number of such bands amounts to  $12N$ . This magnitude will determine the minimum number of basis functions to be allowed for in expansion (10).

## 1.1 Calculation of matrix elements $H_{ij}$

Our calculations are based on the relativistic version of the KKR method [12], and, as usual, the potential is believed to have a *muffin-tin* (MT) form. Then, by virtue of the fact that, outside the MT sphere,  $V(r)$  and  $\Delta V(r)$  are equal to zero, and  $\psi(\mathbf{q}, \mathbf{r})$  are eigenfunctions of operator  $\hat{H}_0$ , the matrix elements (5) can be written as

$$H_{nn'}(\mathbf{q}) = E_n^0(\mathbf{q}) \delta_{nn'} + \tilde{H}_{nn'}(\mathbf{q}) \quad (11)$$

Here

$$\tilde{H}_{nn'}(\mathbf{q}) = \sum_j \int_{\Omega_{MT}} \psi_n^{(j)+}(\mathbf{q}, \mathbf{r}) \left( \Delta V_j(r) \hat{\Sigma}_z \right) \psi_{n'}^{(j)}(\mathbf{q}, \mathbf{r}) d\mathbf{r} \quad (12)$$

In the relativistic KKR method the trial function inside the  $j^{th}$  MT-sphere is chosen as a linear combination of solutions of the Dirac equation in the center-symmetrical field with variational coefficients  $C_{\kappa\mu}^j(\mathbf{k})$

$$\psi^{(j)}(\mathbf{k}, \mathbf{r}) = \sum_{\kappa\mu} i^l C_{\kappa\mu}^{(j)}(\mathbf{k}) \begin{pmatrix} g_{\kappa}^{(j)}(r) \varphi_{\kappa\mu}(\hat{r}) \\ -i f_{\kappa}^{(j)}(r) \varphi_{\bar{\kappa}\mu}(\hat{r}) \end{pmatrix} \quad (13)$$

Here  $\kappa$  is a quantum number such that  $\kappa = l$  if  $\kappa > 0$ , and  $\kappa = -(l+1)$  if  $\kappa < 0$ ;  $\bar{\kappa} = -\kappa$  and  $\varphi_{\kappa\mu}$  are spherical spinors.

$g_{\kappa}^{(j)}(r)$  and  $f_{\kappa}^{(j)}(r)$  are the solutions of the set of radial equations

$$\begin{aligned} g_{\kappa}^{(j)'}(r) &= \left[ 1 + \frac{E - V^{(j)}(r)}{c^2} \right] c f_{\kappa}^{(j)}(r) - \frac{\kappa+1}{r} g_{\kappa}^{(j)}(r) \\ c f_{\kappa}^{(j)'}(r) &= \frac{\kappa-1}{r} c f_{\kappa}^{(j)}(r) - [E - V^{(j)}(r)] g_{\kappa}^{(j)}(r) \end{aligned} \quad (14)$$

$c$  is the velocity of light.

Substituting (13) into (12) yields the following explicit expression for  $\tilde{H}_{nn'}(\mathbf{q})$

$$\begin{aligned} \tilde{H}_{nn'}(\mathbf{q}) = & \sum_j \sum_{\kappa\mu} C_{\kappa\mu}^{jn*} C_{\kappa\mu}^{jn'} \left[ \frac{2\mu}{2\kappa-1} \int_0^{r_{S_j}} r^2 f_{\kappa}^n(r) \Delta V_j(r) f_{\kappa}^{n'}(r) dr - \right. \\ & \left. - \frac{2\mu}{2\kappa+1} \int_0^{r_{S_j}} r^2 g_{\kappa}^n(r) \Delta V_j(r) g_{\kappa}^{n'}(r) dr \right] - \\ & - C_{\kappa+1,\mu}^{jn*} C_{\kappa\mu}^{jn'} \left[ \beta^- \int_0^{r_{S_j}} r^2 f_{\kappa+1}^n(r) \Delta V_j(r) f_{\kappa}^{n'}(r) dr \right] + \\ & + C_{\kappa-1,\mu}^{jn*} C_{\kappa\mu}^{jn'} \left[ \beta^+ \int_0^{r_{S_j}} r^2 g_{\kappa-1}^n(r) \Delta V_j(r) g_{\kappa}^{n'}(r) dr \right] \end{aligned} \quad (15)$$

Here

$$\beta^{\pm} = 2 \sqrt{\frac{\kappa + \mu \pm \frac{1}{2}}{2\kappa \pm 1}} \times \sqrt{\frac{\kappa - \mu \pm \frac{1}{2}}{2\kappa \pm 1}},$$

and  $r_{S_j}$  is the radius of the  $j^{\text{th}}$  MT sphere.

## 2 Computational results

We have calculated the electronic structure of antiferromagnetic Cr for  $\mathbf{Q} = 2/\pi(0, 1, 0)$ . As mentioned above, in this case the unit cell contains two atoms with coordinates  $\mathbf{R}_0 = a/2(0, 0, 0)$  and  $\mathbf{R}_1 = a/2(1, 1, 1)$ , and the magnetic moments equal in magnitude but opposite in direction. As a consequence, at different lattice sites, the spin-polarizing part of potential (18) differs only in sign. The accuracy of the technique was tested by comparing the energy eigenvalues with those obtained within the spin-polarized relativistic KKR (SPRKRR) method [6].

In this paper we used the  $l$ -dependent model potential of the form [16]

$$V_l^s(r) = (2/r)[1 + (Z - 1)/\{H[\exp(r/d_l^s) - 1] + 1\}] \quad (16)$$

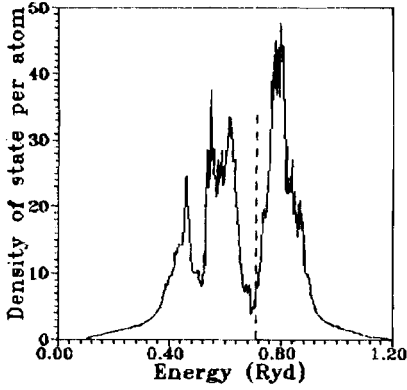
( $H = d_l(Z-1)^{2/5}$ ;  $d_l$  are the potential parameters;  $l$  is the orbital quantum number;  $s$  characterizes the spin direction;  $Z$  is the nuclear charge). Our experience has shown that such a model potential is convenient to use for calculating physical characteristics of metals with a well known electronic structure. In this case, by fitting the parameters  $d_l$ , one reconstructs the electron spectrum estimated *ab initio* which is used for further calculations.

The parameters were fitted according to Kübler's [2] calculations performed non-relativistically; so, while fitting the parameters, we had to use the non-relativistic version of the Green function method with spin polarization. Next, the two parts of the potential were defined as

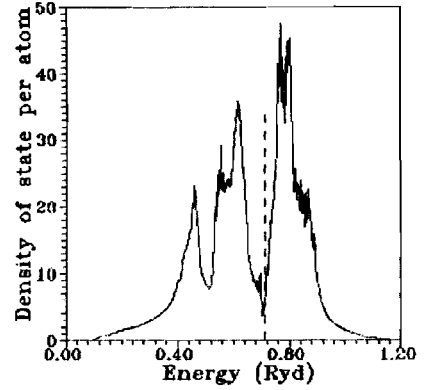
$$\begin{aligned} V &= \frac{1}{2}(V^+ + V^-) \\ \Delta v &= \frac{1}{2}(V^+ - V^-) \end{aligned} \quad (17)$$

In passing to the relativistic version the potential was assumed to be unchanged.

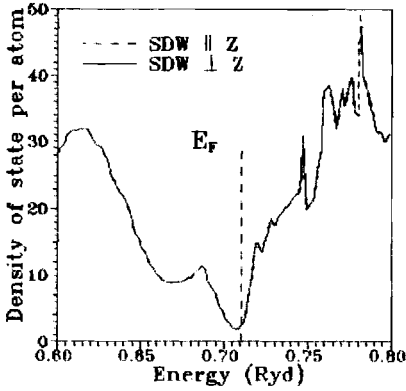
AF Cr with SDW (20 atoms per unit cell)



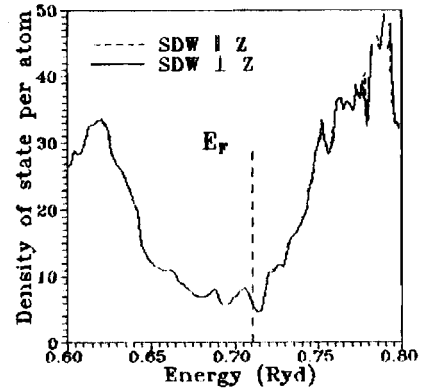
AF Cr with SDW (40 atoms per unit cell)



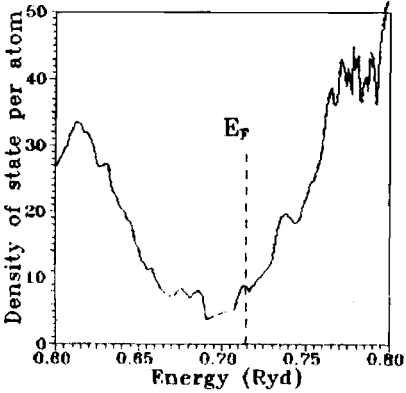
AF Cr with SDW ( 4 atoms per unit cell)



AF Cr with SDW ( 8 atoms per unit cell)



AF Cr with SDW (20 atoms per unit cell)



AF Cr with SDW (40 atoms per unit cell)

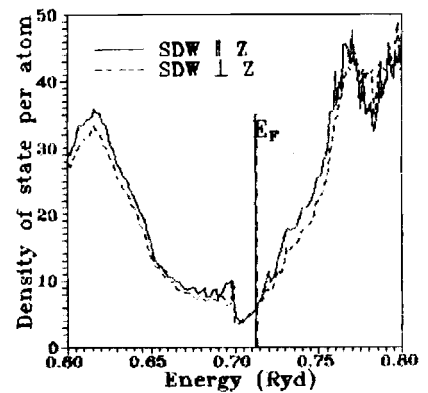
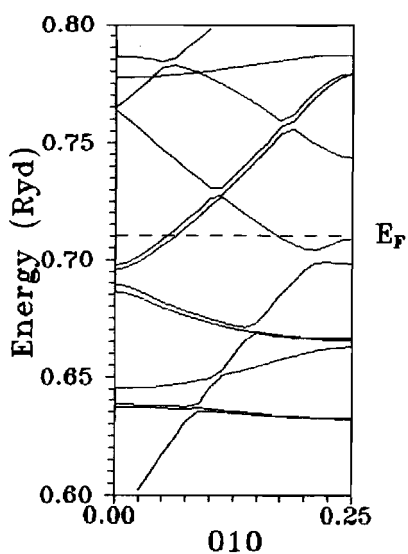
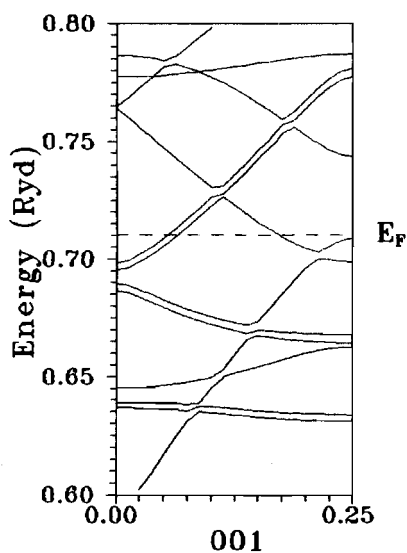


Figure 1.

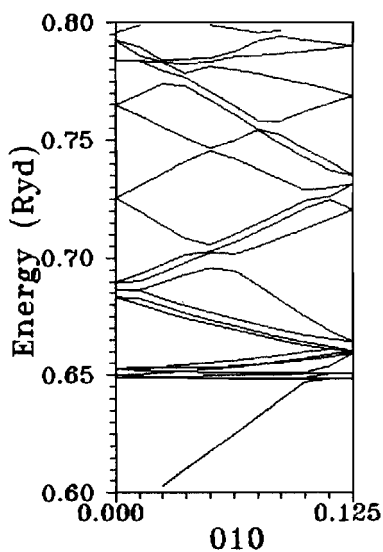
AF Cr SDW  $\perp$   
(4 atoms per unit cell)



AF Cr SDW  $\parallel$   
(4 atoms per unit cell)



NM Cr  
(8 atoms per unit cell)



AF Cr SDW  $\perp$   
(8 atoms per unit cell)

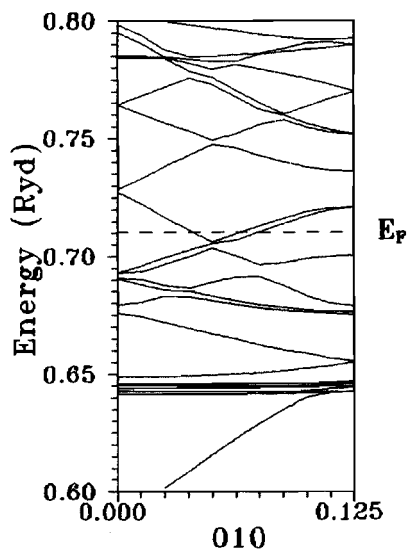
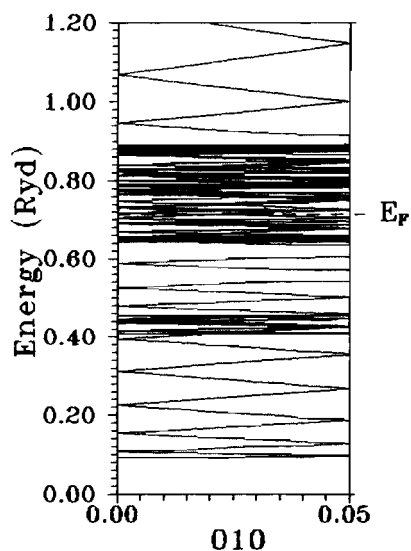
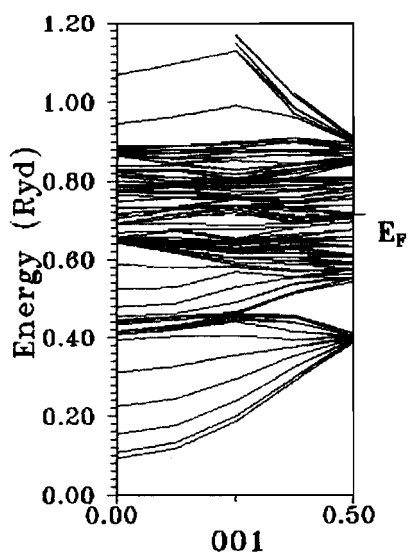


Figure 2a.

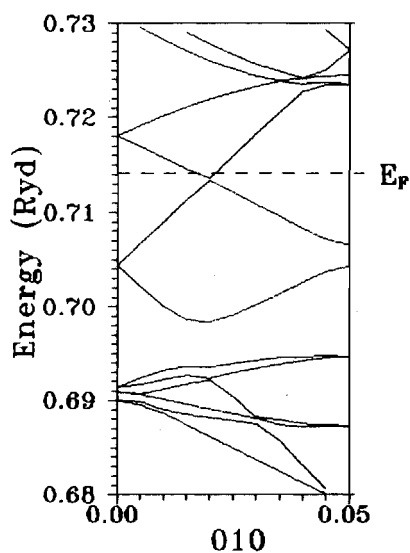
AF Cr SDW  $\perp$   
(20 atoms per unit cell)



AF Cr SDW  $\perp$   
(20 atoms per unit cell)



AF Cr SDW  $\perp$   
(20 atoms per unit cell)



AF Cr SDW  $\perp$   
(20 atoms per unit cell)

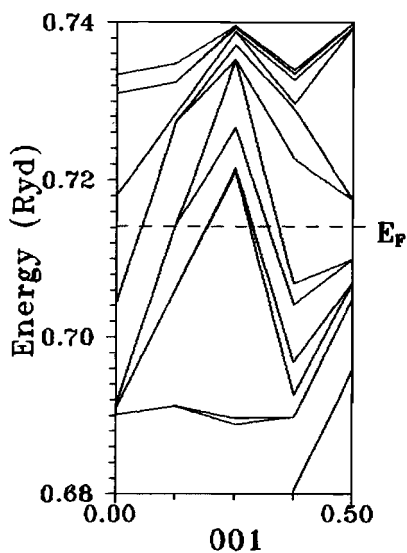
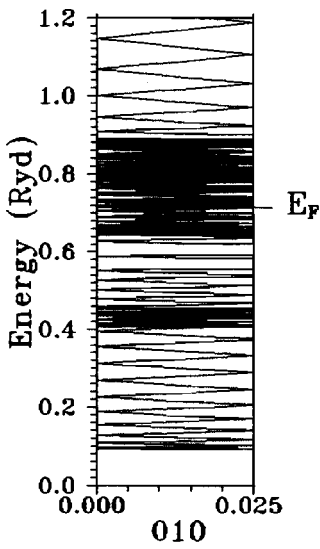


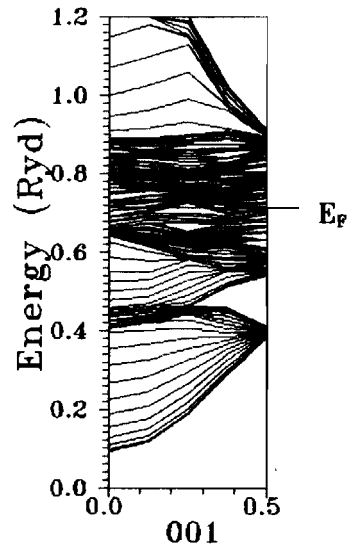
Figure 2b.



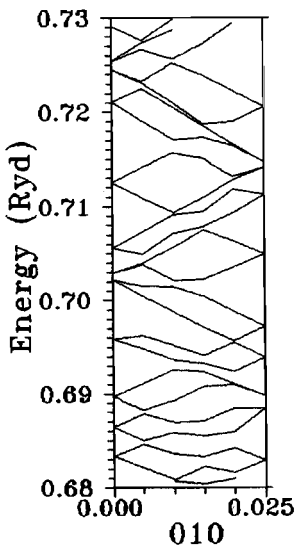
AF Cr SDW  $\perp$   
(40 atoms per unit cell)



AF Cr SDW  $\perp$   
(40 atoms per unit cell)



NM Cr  
(40 atoms per unit cell)



AF Cr SDW  $\perp$   
(40 atoms per unit cell)

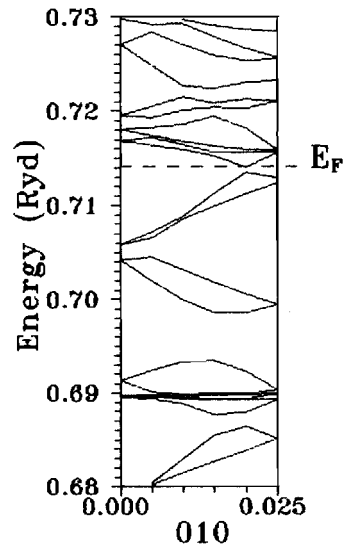


Figure 2c.

Table 1: Electron spectrum of AF *Cr* at points  $\Gamma$  and  $X$  for  $Q = 2\pi/a(0, 1, 0)$  in Ryd. ( as compared with the SPRKKR method )

| Band | Point $\Gamma$ |            | Point $X$     |            |
|------|----------------|------------|---------------|------------|
|      | Present calc.  | SPRKKR [6] | Present calc. | SPRKKR [6] |
| 1    | 0.0924         | 0.0924     | 0.3912        | 0.3911     |
| 2    | 0.4062         | 0.4061     | 0.3968        | 0.3968     |
| 3    | 0.4063         | 0.4061     | 0.5587        | 0.5582     |
| 4    | 0.6429         | 0.6427     | 0.6173        | 0.6172     |
| 5    | 0.6431         | 0.6429     | 0.6565        | 0.6558     |
| 6    | 0.6469         | 0.6467     | 0.6567        | 0.6558     |
| 7    | 0.7860         | 0.7853     | 0.7193        | 0.7192     |
| 8    | 0.7860         | 0.7853     | 0.7196        | 0.7194     |
| 9    | 0.8871         | 0.8869     | 0.8025        | 0.8025     |
| 10   | 0.8872         | 0.8870     | 0.8395        | 0.8395     |
| 11   | 0.8921         | 0.8919     | 0.9005        | 0.9006     |

From here on,  $\Delta V_j(\mathbf{r})$  will be assumed to vary in the magnetic cell as

$$\Delta V_j(\mathbf{r}) = \Delta v(\mathbf{r}) \cos(\mathbf{Q}\mathbf{R}_j), \quad (18)$$

$\Delta v(\mathbf{r})$  being site-independent.

The wave functions of Eq.(2) corresponding to the first twelve energy levels of the valence band were used as basis functions (10). Each energy level of non-magnetic *Cr* being doubly degenerate, the total number of terms in expansion (10) amounted to 24.

The results of calculations for the points  $\Gamma - 2\pi/a(0, 0, 0)$  and  $X - 2\pi/a(0, 0.5, 0)$  of the Brillouin zone are listed in Table 1. It can be seen that the energy eigenvalues differ, on the average, by  $5 \cdot 10^{-4}$  Ryd between the two calculations. Such an accuracy is quite sufficient for most applications. The qualitative picture of the electron spectrum is in complete agreement with our previous SPRKKR calculation.

We have performed a model calculation of the electron structure of AF *Cr* for two types of the unit cell extended along the axes  $Y$  and  $Z$ , which corresponded, respectively, to the longitudinal and transversal spin density waves ( $SDW_{\parallel}$  and  $SDW_{\perp}$ ). Recall that the magnetic moment of the system was  $Z$ -directed. Additionally, we have varied the number of atoms per unit cell:  $N = 2, 4, 8, 20, \text{ and } 40$ , which corresponded to  $\delta = 0, 0.5, 0.25, 0.1, 0.05$ . In all instances the same values of  $V(r)$  and  $\Delta v(r)$  were used. The spin-polarizing exchange part of the potential  $\Delta V(r)$  for different atoms of the unit cell was defined according to (18). The number of terms in expansion (10) amounted to  $12N$ .

Fig.1 plots the density of states for the AF *Cr*. The curves of the electron spectrum are shown in Fig.2

Since the calculation was not self-consistent and a model potential was used, we have calculated only the band contribution to the total energy

$$E_B = \int_{E_F}^{E_F} E N(E) dE \quad (19)$$

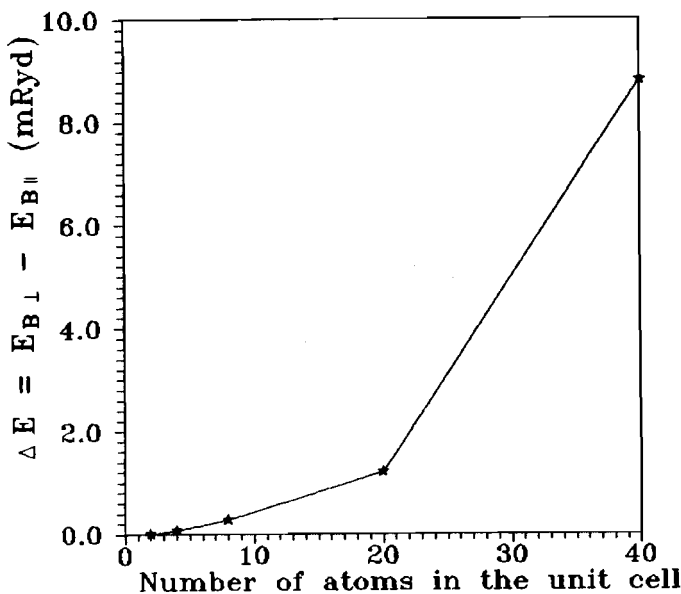


Figure 3.

Fig.3 plots the difference in band energy,  $\Delta E_B = E_{B\perp} - E_{B\parallel}$ , between  $SDW_{\perp}$  and  $SDW_{\parallel}$ , as a function of the number of atoms in the unit cell. As can be seen, in all variants the magnitude of  $(E_B)$  is smaller for the longitudinal SDW.

Although in the relativistic calculation the difference in band energy between different SDW polarizations is insignificant, being actually at the limit of accuracy of our calculation, we can state with a fair degree of assurance that taking into account the relativistic effects in AF Cr results in the fact that the longitudinal and transversal spin-density waves become energetically non-equivalent.

In the nonrelativistic limit (at  $c = 10^{20}$ ) the band contribution to the total energy does not depend on the SDW polarization. This is apparent from Table 2 in which the numerical values of  $E_B$  for a four-atom unit cell are listed. The table also gives the values of the Fermi energy  $E_F$  and the density of states at the Fermi level  $N(E_F)$ .

In our opinion the spin-flip (SF) phase transition occurring in AF Cr may be connected with the electron spectrum anisotropy. This transition, observed in

Table 2: Fermi energy  $E_F$  (Ryd), density of states  $N_{E_F}$  (per cell) and band contribution to the total energy  $E_B$  (Ryd) for  $SDW_{\parallel}$  and  $SDW_{\perp}$  at  $\delta = 0.5$  (four-atom cell). The magnetic moment is  $Oz$ -directed.

|          | Relativistic calculation |                   | Nonrelativistic calculation |                   |
|----------|--------------------------|-------------------|-----------------------------|-------------------|
|          | $SDW_{\perp}$            | $SDW_{\parallel}$ | $SDW_{\perp}$               | $SDW_{\parallel}$ |
| $E_F$    | 0.71032                  | 0.71030           | 0.71656                     | 0.71656           |
| $N(E_F)$ | 9.41893                  | 9.36621           | 10.5092                     | 10.5093           |
| $E_B$    | 12.7067                  | 12.7064           | 12.8857                     | 12.8857           |

AF Cr at 118K , manifests itself in the fact that the longitudinal polarization of the SDW changes to the transversal one. From the standpoint of electronic structure, the nature of such SF transition in chromium is still unclear. Moreover, this transition is unlikely to be explained within the framework of nonrelativistic treatment, the nonrelativistic electron spectrum being identical for the longitudinal and transversal SDW.

Obviously, to discuss the possibility of such a phase transition one should at least carry out a fully self-consistent calculation for different lattice constants.

### 3 Conclusion

Though in this paper we have used the relativistic KKR wave functions as basis functions, the present approach may be easily realized within any existing method for calculating the electron states. This will allow the electronic properties of materials with complex magnetic structure to be readily calculated without loss of accuracy. The present technique, being most efficient for the SDW-type systems, can be also used for helical magnetic structures. In the latter case, however, the spin-polarizing part of potential (18) should be appropriately re-defined.

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# DYNAMICAL PROPERTIES OF Au ADATOMS ON LOW INDEX Cu FACES BY MOLECULAR DYNAMICS SIMULATION

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## INTRODUCTION

In recent years there is a growing interest in the study of vibrational properties of both clean and adsorbate covered surfaces of metals.<sup>1,5</sup> For several years two complementary experimental methods have been used to measure the dispersion relations of surface phonons on different crystal faces. These are the scattering of thermal helium beams<sup>2,5</sup> and the high-resolution electron-energy-loss-spectroscopy.<sup>3,6</sup>

At the same time, many lattice dynamics models have been constructed from force-constant models<sup>1</sup> or ab-initio methods.<sup>7</sup> Recently, the technique of molecular dynamics (MD) simulation has been widely used<sup>8-11</sup> to study vibrations, surface melting, roughening and disordering. In particular, it has been demonstrated<sup>4,10,11</sup> that the presence of adatoms modifies drastically the vibrational properties of surfaces. Lately, the dynamical properties of Cu adatoms on Cu(100)<sup>12</sup> and Cu(111)<sup>13</sup> faces have been calculated using MD simulations and a many-body potential based on the tight-binding (TB) second-moment approximation (SMA).<sup>14-16</sup>

The aim of the present paper is to extend the previous work<sup>12,13</sup> to different adsorbate than the substrate. We have thus studied the vibrational properties of Au single adatoms on the low-index faces of copper, and compared the present results with the above studies. The choice of Au comes from the fact that the Cu-Au alloys have been widely studied and used as prototype by many groups.

## MODEL AND METHOD OF COMPUTATION

The atomic interactions of the system are derived from a many-body empirical potential, the attractive part of which is expressed within the SMA of the TB theory<sup>14-16</sup>, while the repulsive term is a pair-potential of Born-Mayer type. Accordingly, the total energy of the system is written as:

$$E = - \sum_{i=1}^N \left( \sum_{j=1}^N A_{\alpha\beta} \exp[-p_{\alpha\beta}(\frac{r_{ij}}{r_o^{\alpha\beta}} - 1)] - \left\{ \sum_{j=1}^N \xi_{\alpha\beta}^2 \exp[-2q_{\alpha\beta}(\frac{r_{ij}}{r_o^{\alpha\beta}} - 1)] \right\}^{1/2} \right) \quad (1)$$

where  $r_o^{\alpha\beta}$  is the nearest-neighbor distance in the pure metals if  $\alpha=\beta$  or in the ordered alloy if  $\alpha \neq \beta$ ,  $N$  is the number of the particles and the potential includes interactions up to 5th neighbors. The parameters  $A_{\alpha\beta}$ ,  $\xi_{\alpha\beta}$ ,  $p_{\alpha\beta}$ , and  $q_{\alpha\beta}$  have been fitted to reproduce at  $T=0^\circ\text{K}$  the experimental values of cohesive energy, equilibrium condition, and elastic constants of the pure elements and of the compound  $\text{Cu}_3\text{Au}$  and are given in Table 1.<sup>17,18</sup> As it has been demonstrated in Ref. 18, these adjustable parameters predict also satisfactorily properties of the ordered alloys  $\text{CuAu}_3$  and  $\text{CuAu}$ ; they can thus be used to describe interactions between the single Au adatoms and Cu atoms of the substrate.

**Table 1.** Potential parameters

| $\alpha\beta$ | $A_{\alpha\beta}$ (eV) | $\xi_{\alpha\beta}$ (eV) | $p_{\alpha\beta}$ | $q_{\alpha\beta}$ | $r_o^{\alpha\beta}$ (Å) |
|---------------|------------------------|--------------------------|-------------------|-------------------|-------------------------|
| Cu-Cu         | 0.0869                 | 1.2291                   | 10.83             | 2.282             | 2.5466                  |
| Cu-Au         | 0.2300                 | 1.8093                   | 9.44              | 3.425             | 2.6375                  |

The MD simulations have been carried out in the microcanonical ensemble and the system was made up of 2560, 2800 and 2880 Cu particles arranged on a fcc lattice with (100), (110), and (111) faces respectively. Periodic boundary conditions were imposed in the three space directions. The free surfaces were produced by fixing the dimensions of the simulation box at a value twice as large as the thickness of the crystal along the z-direction; an infinite slab was thus produced delimited by two free surfaces. The equations of motion were integrated by means of the Verlet algorithm and a time step  $\delta t = 5 \times 10^{-15}$  s. With this integration step the total energy was conserved within  $\delta E/E = 10^{-5}$ . Initially, 5000 time steps were used to reach thermal equilibrium, while another 10000 steps were subsequently taken to calculate time-averages.

In order to study the vibrational properties of a single Au adatom on Cu faces, one adatom was placed on each face of the slab. Simulations were performed in the range of 300-1000°K to deduce the temperature dependence of the various quantities. The value of the lattice constant was adjusted, at each temperature, so as to result in zero pressure for the bulk system, while the atomic MSD's were determined on a layer by layer basis from equilibrium averages of the atomic density profiles. Furthermore, the phonon DOS of Au adatom was obtained from the Fourier transform of the velocity autocorrelation function<sup>12</sup>.

## RESULTS AND DISCUSSION

### Phonon DOS

In figures 1, 2, and 3 we present the phonon DOS of Au single adatoms on Cu(100), Cu(110), and Cu(111) respectively for the three directions x, y, and z at 300°K. It is interesting to note that the structure and position of these modes are completely different from those of the corresponding clean surfaces of Cu<sup>12,13</sup>.

In figure 1 the DOS along the  $[1\bar{1}0]$  or  $[110]$  directions (solid and dashed line respectively, parallel to the surface) shows two pronounced peaks at 1.25 and 1.6 THz, while for Cu adatoms on Cu(100) a single peak at 2.0 THz was found<sup>12</sup>. This shift towards lower frequencies is somewhat expected, because the Au adatom is heavier than the Cu atom. The DOS at the normal direction (thick dashed line in Figure 1) shows a main peak at

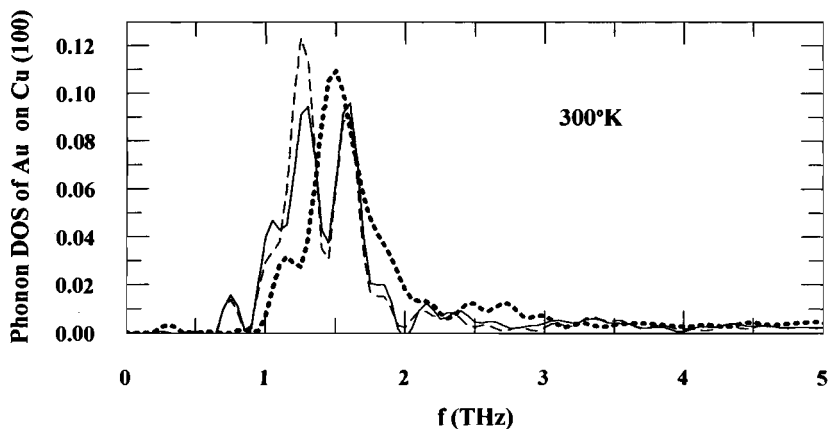


**Figure 1.** Phonon density of states of Au adatom on Cu (100) at 300°K; solid line: along the  $[1\bar{1}0]$  direction, dashed line: along the  $[110]$  direction, thick dashed line: normal to the surface.

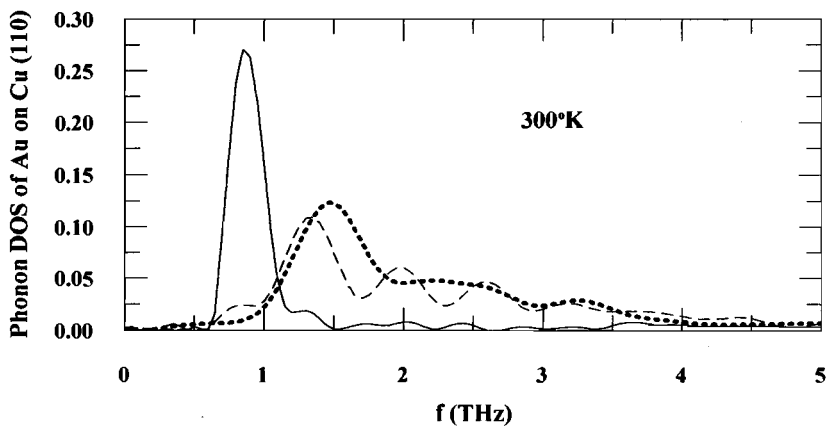


**Figure 2.** Phonon density of states of Au adatom on Cu (110) at 300°K; solid line: along the  $[1\bar{1}0]$  direction, dashed line: along the  $[001]$  direction, thick dashed line: normal to the surface.

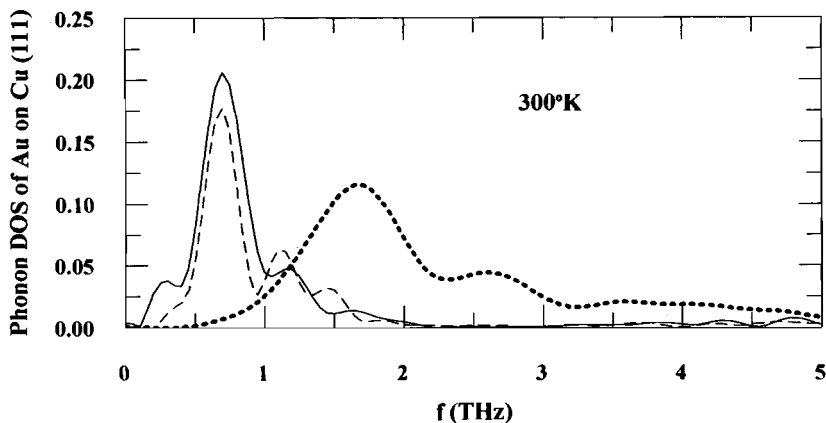


**Figure 3.** Phonon density of states of Au adatom on Cu (111) at 300°K; solid line: in-plane x-direction, dashed line: y-direction, along the  $[110]$ , thick dashed line: normal to the surface.

1.5 THz, while the corresponding mode for Cu adatoms was situated at 2.4 THz<sup>12</sup>. We notice also that the peaks of Cu adatoms, which were found at higher energies, are now absent, denoting a rather weaker coupling of Au adatom with the surface atoms, than that of Cu adatom with the same face.

Concerning the phonon DOS of Au adatom, on Cu(110) (Figure 2), we observe a main peak at 0.85 THz for the  $[1\bar{1}0]$  direction (solid line), parallel to the nearest-neighbor rows (compared to 1.1 THz for the Cu adatom), while for the other in-plane direction parallel to  $[001]$  (dashed line) the dominant mode is at a higher frequency, 1.35THz. This is compatible with the fact that the Au adatom is less bound along the  $[1\bar{1}0]$  direction (parallel to the channels of (110) face), than along the  $[001]$  direction across the channels. Furthermore, the DOS at the normal to the surface direction (thick dashed line in Figure 2) shows a broad peak at 1.45THz.

In the case of Cu(111) face, the Au adatom presents almost similar phonon modes for both the in-plane directions (solid and dashed line in Figure 3) at 0.7THz, which can be compared with that of Cu adatom on the same surface (1.1THz). There is now again a shift to lower frequencies, due to the different mass of the two elements. The DOS at the perpendicular to the surface direction ( thick dashed line in Figure 3) shows a main peak at 1.7 THz, which appears in energetically lower position, compared with that of Cu adatom (3.2 THz)<sup>13</sup>.

The above features indicate that for the parallel to the surface directions the weakest coupling between the Au adatom and the surface atoms occurs for the (111) face, while the strongest for the (100) surface. However, the opposite happens for the normal to the surface direction. In addition, the phonon modes of Au adatom are found in lower frequencies than those of Cu adatom.

### Mean-square-displacements

The temperature dependence of the mean-square-displacements of Au adatom in the normal to the surface direction is shown in Figure 4 for the three low-index faces of Cu. We note that up to 500°K the MSD's on the three different faces are almost equal, while at higher temperatures the vibrational amplitudes of Au on Cu(110) present enhanced anharmonicity and become much larger than on the other faces. These results denote that

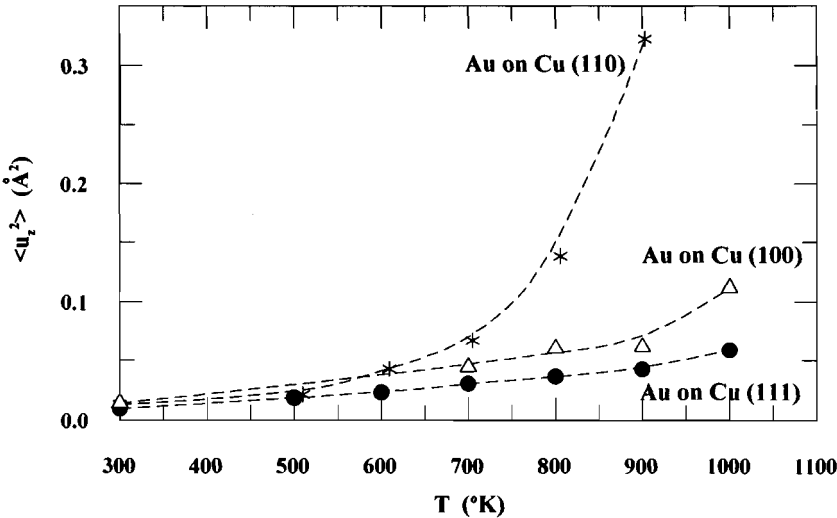


Figure 4. Mean-square-displacements of Au adatom in the normal to the surface direction as a function of temperature, for the three low-index faces of Cu.



the Au adatom is less tightly bound in z-direction on the (110) and more on the (111) face, which is compatible with the behavior of the adatom phonon DOS in the same direction. Furthermore, a comparison of MSD's of the Au adatom with those of the Cu adatoms<sup>13,19</sup> in the temperature range 300-1000°K reveals that the two adatoms have almost the same values on the corresponding Cu faces.

### Relaxations of Au adatom

We have also deduced from our simulations the relaxed positions of Au adatom in the perpendicular to the surface direction. In Figure 5 we give the percentage relaxation of Au on the low-index faces of Cu, with respect to the bulk interlayer spacing of the latter, as a function of temperature. We observe at room temperature, an important contraction of the relaxed position of Au adatom ( $\cong 16\%$ ), which is more pronounced than in the case of Cu adatom<sup>13</sup> ( $\cong 11\%$ ). As the temperature increases, the adatom presents stronger contractions on Cu(110) than on the other faces, in agreement with the MSD results, attaining at 1000°K a value of -60%.

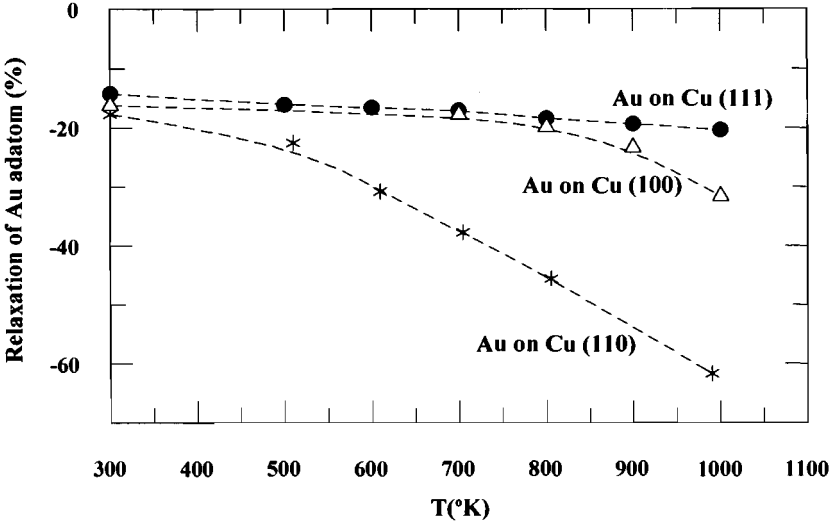


**Figure 5.** Temperature dependence of percentage relaxation of Au adatom on the low-index faces of Cu with respect to the bulk interlayer spacing.

### CONCLUSIONS

We have studied the vibrational properties of Au adatoms on the low-index faces of copper. From the position of new phonon modes, which are due to the presence of the adatom, it comes out that the gold adatom is weakly coupled with the atoms of Cu(111) for the directions parallel to the surface and tightly bound with those of Cu(100). These modes are found in lower frequencies than those of the Cu adatom. The temperature dependence of MSD's and relaxed positions of the Au adatom along the normal to the surface direction, reveal that this atom is more tightly bound with the (111) face and less with the (110) face.

It would be of great interest to experimentally verify these new results of phonon modes, MSD's and relaxations by suitable methods, such as electron-energy-loss-spectroscopy or thermal helium beam scattering.

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## NMR SPECTROSCOPIC INVESTIGATIONS OF SURFACE AND INTERLAYER SPECIES ON MINERALS, CLAYS AND OTHER OXIDES

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### INTRODUCTION

The behavior of chemical species adsorbed on solid surfaces and exchanged into clay interlayers plays a significant role in controlling many natural and technologically important processes, including rheological behavior, catalysis, plant growth, transport in natural pore fluids and those near anthropogenic hazardous waste sites, and water-mineral interaction. Adsorption and exchange reactions have been the focus of intense study for many decades (see, e.g., references 1-6 for introductions). Only more recently, however, have there been extensive spectroscopic studies of surface species (e.g., references 7-11). Among the spectroscopic methods useful for studying surface and exchanged species (e.g., infrared, X-ray photoelectron spectroscopy [XPS] and X-ray absorption spectroscopy [XAS]), nuclear magnetic resonance spectroscopy (NMR) has the considerable advantage of providing not only structural information via the chemical shift and quadrupole coupling constant but dynamical information in the Hz - mHz range via lineshape analysis and relaxation rate measurements.<sup>7,12-14</sup> It is also possible to obtain data in the presence of a separate fluid phase, which is essential for many applications. This paper illustrates the range of applications of NMR methods to surface and exchanged species through review of recent work from our laboratory on Cs in clay interlayers and Cs, Na and phosphate adsorbed on oxide surfaces. The substrate materials used for these experiments and our long-term objectives are related to problems of

geochemical interest, but the principles and techniques are of fundamental interest and applicable to a wide range of technological problems.

#### INTERLAYER EXCHANGED Cs

Cations exchanged into the interlayers of expandable clays (smectites)<sup>15</sup> are comparatively easy to study with NMR methods because the cations become major components of the phase and their concentrations are often several wt %. In addition to Cs; Li, Na, K, and Cd have been studied by NMR.<sup>16-21</sup> We have chosen to investigate <sup>133</sup>Cs because it is a significant component of nuclear waste, because it provides an end-member case as the least electronegative cation, and because it has desirable nuclear properties (100% abundance, relatively high frequency, 65.5 MHz at  $H_0 = 11.7$  T, and small quadrupole moment).<sup>22-24</sup>

Clays are ubiquitous in near surface geological environments and are used in a wide range of technological applications. Because many of them have large cation exchange capacities they greatly affect cation reactivity and transport in natural and hazardous waste environments, and they have found application as, e.g., sorbants and molecular sieves. The environments and dynamical behavior of interlayer cations have proven difficult to study directly, because most clays lack long-range order and, thus, the interlayer sites are poorly probed by diffraction methods. In contrast, NMR provides a direct probe of the local cation environments and their dynamical behavior.

The <sup>133</sup>Cs NMR behavior of Cs-exchanged smectites illustrates well the kinds of information that can be obtained.<sup>22-24</sup> Smectites are phyllosilicates similar in some ways to micas. They have layer structures consisting of a sheet of octahedral sites sandwiched between two sheets of tetrahedral sites, the so called TOT or 2:1 structure. In most smectites the tetrahedral sites are occupied by Si and the octahedral sites by Al, Fe, Mg, Li and other cations. The TOT layers develop net negative charge by aliovalent substitution in both the octahedral and tetrahedral sites, causing the attraction of cations and water molecules into the interlayer regions. Cation exchange can be quite rapid, because the interlayer regions are two dimensional and exposed to exterior fluids.

We have done our experiments with hectorite, which is a 2:1 smectite that develops negative layer charge by substitution of Li for Mg in the octahedral sheet.<sup>22,23</sup> Samples were prepared by multiple exchange in 1.0 and 0.1 M CsCl solutions until essentially complete Cs-exchange was reached (97% of the interlayer cations). Temperature dependent data are essential to interpret the results, because there is rapid exchange of Cs among different interlayer sites at room temperature (RT).

At temperatures greater than -10°C, the <sup>133</sup>Cs NMR spectrum of a Cs-exchanged hectorite in contact with 1.0M CsCl solution (a slurry sample) consists of two peaks, one between 3.5 and

10.9 ppm and the other between -15.2 and -8.3 ppm (Figure 1). These peaks are readily assigned to Cs in the CsCl solution (positive peak) and Cs in the clay interlayer (negative peak). With decreasing temperature the peak for the solution disappears between -30 and -40°C as the solution freezes and CsCl precipitates (peak at 228.1 ppm). The peak for Cs in the interlayer begins to split into two peaks at about -20°C, which at temperatures less than -70°C have values near 27 and -29 ppm. Such peak splitting is classical behavior for dynamical averaging between two sites, and the spectra can be used to determine frequencies of exchange between these two sites via line shape analysis. The two peaks are resolved at low temperature, because Cs is either not exchanging between the two sites or is doing so at frequencies an order of magnitude or more less than the peak separation, which is in the kHz range. As Cs atoms begin to exchange between the two sites with increasing temperature their nuclei take on a chemical shift that is the abundance weighted average for the two sites. Complete averaging occurs when the exchange frequency is approximately an order of magnitude greater than the peak splitting (ca. 10 kHz here). For our sample, averaging appears to begin near -70°C and to be complete for most Cs near -20°C. There is some site heterogeneity, as can be expected for a complex natural sample.

The two interlayer sites at low temperatures are assigned to Cs tightly bonded to the oxygens of the basal surface (near -29 ppm) and to Cs less tightly bonded to the basal oxygens and located more in the center of the interlayer (near 27 ppm). For both of these types of sites, the Cs is also coordinated by water molecules. The water keeps the TOT layers separated and is also undergoing site exchange. Thus, space is available for the Cs to move among sites. The frequency of this motion, however, is orders of magnitude less than typical lattice vibrational frequencies and is probably best thought of as self-diffusion coupled to the motion of the water molecules.

The dynamical behavior of the slurry sample contrasts dramatically with the rigid Cs observed for a fully dehydrated Cs-exchanged hectorite (Figure 2). In the absence of interlayer water, Cs is present in two sites coordinated only by basal oxygens. These are probably 9-coordinate (near 30 ppm) and 12-coordinate (near -120 ppm). The other peaks in the spectra are spinning sidebands, which are the result of magic angle spinning and a relatively large site asymmetry unaveraged by atomic motion.

The results for the hectorite slurry sample also contrast with those for a Cs-exchanged vermiculite. Vermiculite is a 2:1 clay mineral that develops its layer charge primarily by Al for Si substitution in the tetrahedral sheet. The total substitution is also much greater than in smectites. Thus, the amount of negative charge and the distance to the interlayer cation from the site of charge development is much less in vermiculites than in hectorite. The net effects for vermiculite are that interlayer Cs causes the interlayer region to dehydrate and collapse, forcing Cs to occur in only one site (near 57 ppm, data not shown) and preventing any dynamical behavior near room temperature.

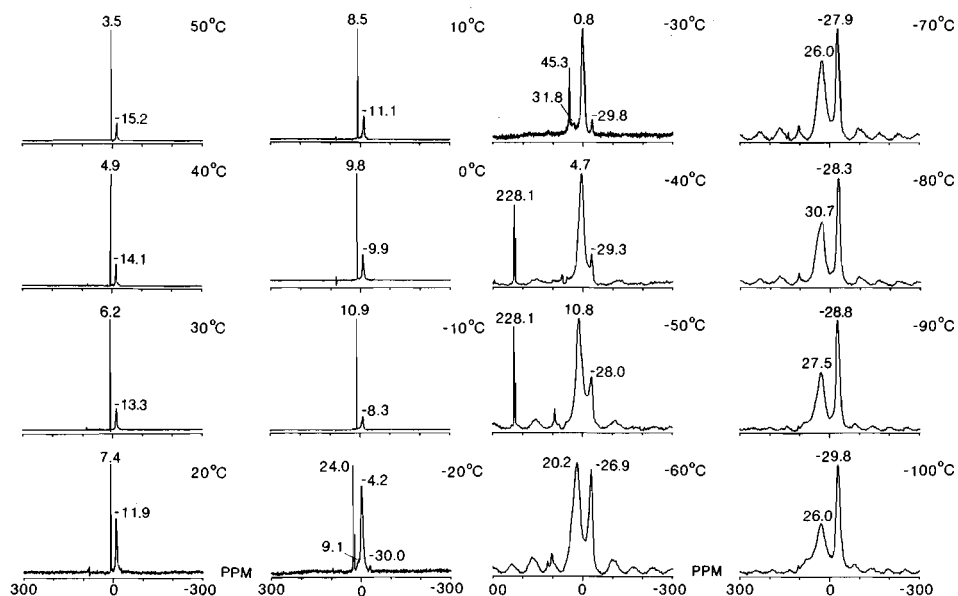


Figure 1.  $^{133}\text{Cs}$  MAS NMR spectra of Cs-exchanged hectorite in a 1.0 M CsCl slurry at temperatures between, 50 and  $-100^\circ\text{C}$ . The  $H_0$  field strength was 8.45 T. After reference 22.

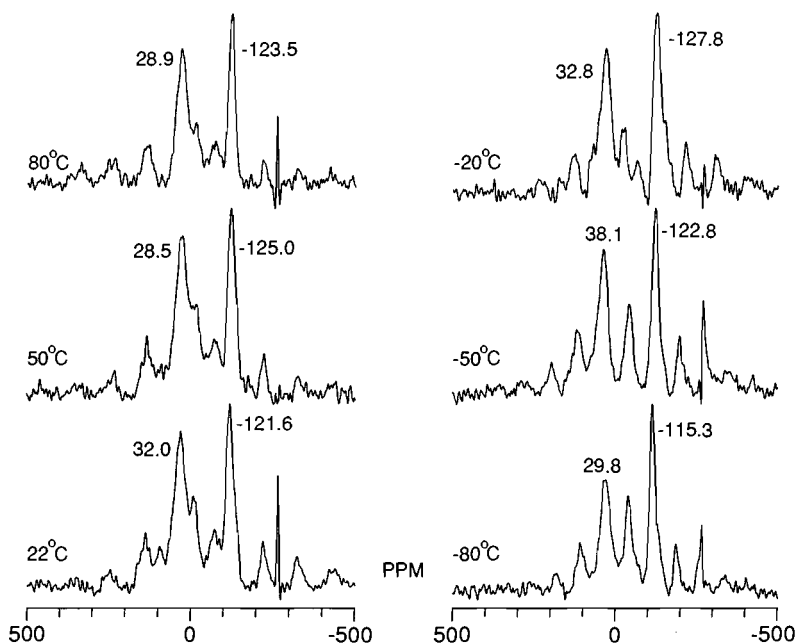


Figure 2.  $^{133}\text{Cs}$  MAS NMR spectra of Cs-exchanged hectorite sample dehydrated at 500°C before analysis at temperatures from 80 to  $-80^\circ\text{C}$ . The labeled peaks near -120 and +30 ppm are true center bands, and the other peaks are spinning sidebands. After reference 22.

Cations adsorb on solid surfaces for the same fundamental reason that they exchange into clay interlayers or zeolitic cavities, that is, to balance local negative charge. The molecular scale mechanisms of surface adsorption, however, can be significantly different. In clay interlayers all the oxygen atoms of the basal surface are 2-coordinate by tetrahedral cations (Si,Al). Some exterior surfaces are structurally similar to clay interlayers, e.g., the basal surfaces of clay particles, but many surfaces are very different, containing large numbers of broken bonds and locally uncompensated charge. pH dependent hydrogen adsorption/desorption greatly affects surface charge, with positive charge occurring at low pH and negative charge at high pH. The details vary greatly with bulk phase composition. For large, low-charge cations such as Cs, the presence or absence of a bulk aqueous phase and relative humidity (RH) have important effects. At low RH there are few water molecules on the surface, and the cations must interact directly with the surface oxygens. As RH increases the equilibrium number of surface water molecules increases, and at RHs approaching 100% there is a surface film many molecules thick that behaves like bulk water. For typical phyllosilicates (kaolinite and mica) there are 1, 2, and 3 statistical monolayers of adsorbed water at 10%, 60% and 80% RH respectively.<sup>25,26</sup>

The <sup>133</sup>Cs NMR results for Cs on the surfaces of illite, kaolinite, boehmite and silica gel (Figure 3) show that for this large, low charge cation the surface behavior is quite similar to the interlayer behavior. They also illustrate the capabilities of NMR methods to probe surface species and the effects of RH on the structural environments and dynamical behavior of the Cs.<sup>24,27</sup> The samples were prepared by immersing 0.5 gm of powdered solid in 50 ml of 0.1M CsCl solution at 25°C for 5 days. Final pHs were between 4.60 and 7.77, greater than the zero point of charge, except for boehmite, which has a ZPC of ca. 8.0.<sup>28</sup> The solution was removed from the samples by filtering through a millipore filter with no washing except when indicated. The extent of removal of the solution varies among the samples due to varying permeability and significantly affects the spectra. Silica gel is an amorphous, high surface hydrous silica. Illite is a 2:1 phyllosilicate with a composition approaching muscovite mica and little interlayer exchange capacity. Kaolinite is a 1:1 phyllosilicate with a sheet of tetrahedra occupied by Si linked to a sheet of octahedra occupied primarily by Al. Boehmite is  $\gamma$ -AlO(OH) and has a layer structure based on Al-O,OH octahedra.

For boehmite (Figure 3D) the solution was removed very effectively by filtering, and only those Cs atoms tightly bound to the surface (Stern layer)<sup>6</sup> are preserved in the sample. The amount of adsorbed Cs is small (ca. 0.0016 atoms/Å<sup>2</sup>), as expected at pHs less than the ZPC. At ca. 0% RH (over solid P<sub>2</sub>O<sub>5</sub>) there is one broad peak due to Cs in asymmetrical environments coordinated by surface oxygens and what few water molecules are on the surface. At higher RHs, the peaks are much narrower, indicative of Cs in very symmetrical, time-averaged environments coordinated to both surface oxygens and water molecules and probably undergoing exchange among sites at

frequencies > ca. 10 kHz. The chemical shifts become less positive as the surface  $\text{Ca}/\text{H}_2\text{O}$  ratio decreases, paralleling the variation in bulk solutions.<sup>29</sup>

For the silica gel (Figure 3A), the solution was removed slightly less effectively, and more Cs was left (ca. 0.0020 atoms/Å<sup>2</sup>). The spectral behavior is quite similar to that of boehmite, except that there is a peak due to surface Cs coordinated by only water molecules and not in contact with the surface oxygens (so-called outer sphere complexes)<sup>2,3</sup> at 30% RH. Complete dynamical averaging among sites at frequencies greater than ca. 10 kHz occurs at 70% RH and greater.

For illite (Figure 3B) the total amount of Cs adsorbed is two orders of magnitude larger (ca. 0.26 atoms/Å<sup>2</sup>) due primarily to the permanent charge developed by substitution of Al for Si in the tetrahedral sites and to less efficient filtering of the solution caused by lower sample permeability. The maximum amount of hydrated Cs that can be accommodated on the illite surface is ca. 0.023 atoms/Å<sup>2</sup>, close to the amount

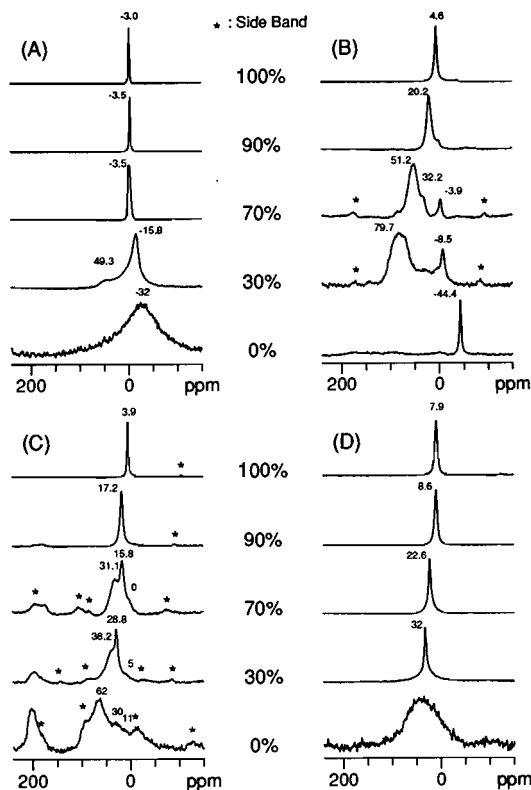


Figure 3. <sup>133</sup>Cs MAS NMR spectra of Cs-exchanged (A) silica gel, (B) illite, (C) kaolinite, and (D) boehmite collected at  $H_0 = 11.7$  T, room temperature and the indicated relative humidities. The peaks marked by \* are spinning sidebands. After reference 27.



expected if the narrow, most negative peak and its small shoulder are due to Cs in direct contact with the surface oxygens (inner sphere complexes).<sup>2,3</sup> The remainder of the Cs is in outer sphere complexes and gives rise to the larger more positive peaks. The illite crystallites are blocky, allowing both inner sphere and outer sphere Cs to adsorb on the crystallite tops and bottoms and on the broken edges of the sheets at the crystallite edges. At 30% RH, the inner sphere complexes resonate at -8.5 ppm (crystallite tops and bottoms) and near 0 ppm (crystallite edges), whereas the outer sphere complexes resonate at ca. 80 ppm (broad peak, tops and bottoms) and near 30 ppm (broad peak, edges). Assignment of these peaks is based on the dependence of the chemical shifts on solid composition, solution composition, behavior on washing with DI water, and comparison with the results for smectites. As for the other samples, dynamical averaging at frequencies > ca. 10 kHz occurs at higher RHs.

For kaolinite the sample permeability was very low and the solution was poorly removed. The spectra (Figure 3C) are consequently complex, containing peaks for inner and outer sphere complexes, CsCl precipitate from residual solution (near 200 ppm) and a complex spinning sideband pattern. Spectral resolution is poorer, but at 70% RH for instance, inner sphere complexes resonate near 16 ppm and outer sphere complexes near 31 ppm. Dynamical averaging of the inner and outer sphere complexes occurs at 70% RH, and at 100% RH even the CsCl precipitate is dissolved in the water film and averaged.

Assignment of the observed peaks just described parallels that for Cs in smectite interlayers.<sup>22,23</sup> Peaks that are more shielded (negative), narrower, vary less with sample condition, vary more with sample composition, and have larger sidebands

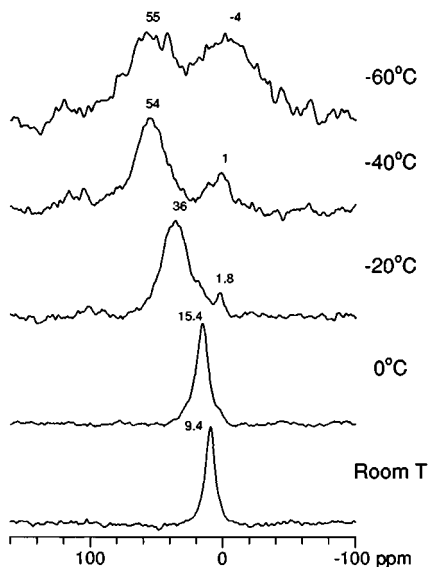


Figure 4.  $^{133}\text{Cs}$  MAS NMR spectra of Cs-exchanged illite equilibrated at 100% relative humidity.  $H_0 = 11.7$  T. Temperatures as labeled. After reference 27.

are assigned to Cs in inner sphere complexes. Peaks that are broader, less shielded, and that vary more with sample condition are assigned to Cs in outer sphere complexes.

The spectral behavior with varying temperature, sample washing and varying solution concentration provides strong confirming evidence for the assignments and also additional dynamical information. Variable temperature data for illite at 100% RH (Figure 4) show that dynamical averaging at frequencies > ca. 1 kHz ceases near -20°C. At lower temperatures more Cs is transferred to inner sphere complexes (the more negative peak) as few water molecules remain on the surface due to freezing. The peaks also become broad, indicating statically asymmetric sites.

For illite and kaolinite with decreasing solution concentration (Figure 5) there are two important changes. The relative intensity for inner sphere complexes increases, and the chemical shifts become substantially less positive or more negative due to the reduced Cs/water ratio, especially for the outer sphere complexes. Washing with DI water removes most of the Cs in outer sphere complexes and causes spectral changes parallel to those caused by decreasing solution concentration (data not shown).

#### Na ADSORPTION ON SURFACES AND COMPETITION WITH Cs

The surface behavior of Na is similar to that of Cs, except that inner sphere complexes are not observed. Although Na has the same charge as Cs, it has a smaller ionic radius and thus a larger hydration energy. Consequently, Na retains its shell of hydration waters. For illite (Figure 6), outer sphere complexes resonate between -7.7 and -1.1 ppm and NaCl

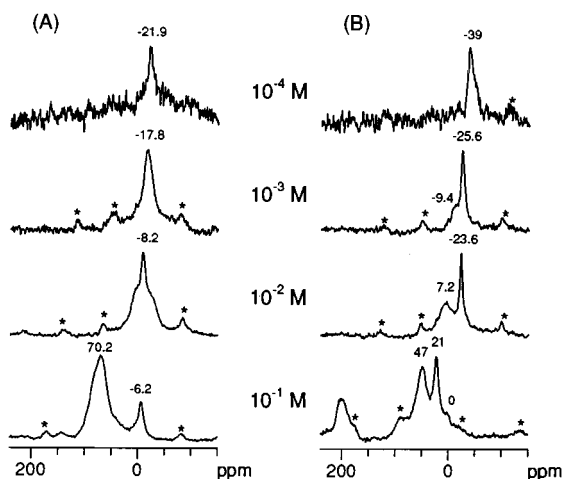


Figure 5.  $^{133}\text{Cs}$  MAS NMR spectra of (A) illite and (B) kaolinite Cs-exchanged at the indicated CsCl solution concentrations and collected at room humidity (ca. 35% RH) and  $H_0 = 11.7$  T. After reference 27.

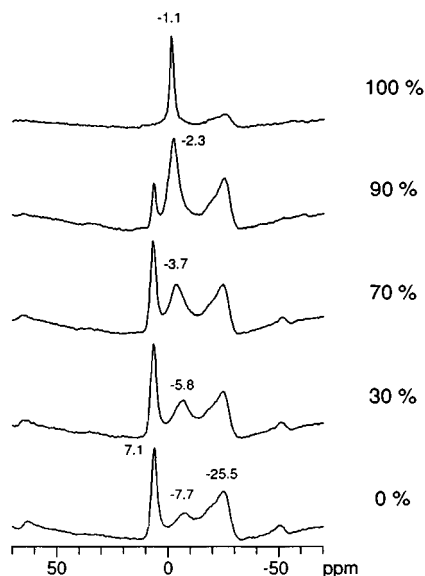


Figure 6.  $^{23}\text{Na}$  MAS NMR spectra of illite exchanged in 0.1 M NaCl solutions at 25°C. Spectra collected at  $H_0 = 11.7$  T, room temperature, and room humidity (ca. 35% RH).

precipitate from residual solution occurs at 7.1 ppm. The peak at -25.5 ppm and the shoulder near -20 ppm are due to unexchangeable Na bound in the illite, as shown by spectra for non-exchanged samples. With increasing RH at RT the relative amount of Na in the surface water film increases, and the amount of NaCl precipitate decreases, as expected for an increasing thickness of the water film. The peak for the surface Na also narrows, indicating increased dynamical averaging of sites. For mixed Cs/Na solutions, the relative amount of Cs in inner sphere sites increases with decreasing Cs/Na ratio, indicating that Cs competes for sites next to the surface (the Stern layer) more effectively than Na (data not shown).

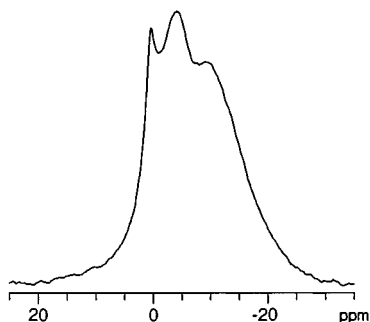


Figure 7.  $^{31}\text{P}$  MAS NMR spectrum of a  $\gamma$ -alumina sample in a 0.1 M  $\text{KH}_2\text{PO}_4$  solution at pH 5.

The structural environments and dynamical behavior of surface phosphate species contrasts strongly with those of Cs and Na described above. For Al-containing substrates, phosphate forms strongly bonded inner sphere complexes through P-O-Al linkages. Our work on the <sup>31</sup>P NMR behavior of kaolinite, boehmite, and  $\gamma$ -alumina reacted at 25°C for 24 hrs with KH<sub>2</sub>PO<sub>4</sub> solutions with concentrations from 10<sup>-1</sup> to 10<sup>-4</sup> M and pHs from 3 to 11 are consistent with this idea but also indicate that amorphous K-H-aluminophosphate precipitates form under all conditions examined). The absence of dynamical averaging is clearly indicated by the spectrum of a moist  $\gamma$ -alumina sample (Figure 7). The narrow peak near +2 ppm is due to phosphate in the solution, that near -5 ppm to inner sphere complexes, and that near -12 ppm to amorphous precipitates. The chemical shifts of the inner sphere complexes become less negative with increasing pH, consistent with progressive deprotonation with increasing pH and rapid H-exchange among surface phosphate sites.

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## SONOCHEMICAL SYNTHESIS OF AMORPHOUS BIMETALLIC Fe-Ni ALLOYS

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### INTRODUCTION

The amorphous alloys often called metallic glasses or glassy metals, obtained by rapid quenching of the melt lack the long range order of their crystalline counterparts and are of great importance in modern technology because of their unique electronic, magnetic and corrosion resistant properties<sup>1-4</sup>. Ferromagnetic amorphous alloys containing Fe and Co show excellent magnetic properties equivalent or superior to the conventional soft magnetic materials and they have already being used in magnetic storage media and power transformer core<sup>5</sup>. The acoustic cavitation, *i.e.*, the formation, growth and implosive collapse of a bubble in liquid generate transient localized hot spot; a temperature of 5000 K with sub-microsecond life time and a pressure of 1800 atm. is achieved with cooling rate  $> 10^9 \text{ K}^{-6-8}$ . This extremely rapid cavitation cooling rate is much faster than that obtained by other conventional techniques like spalt quenching or roller quenching<sup>9</sup>. Suslick *et al* have employed this sonochemical method for the preparation of nanosized amorphous metallic powders of Fe, Co and their alloys, and metal carbide,  $\text{Mo}_2\text{C}$ <sup>10-14</sup>. The important criterion for achieving the good sonochemical yield is that the precursor should be volatile, because the primary sonochemical reaction site is the vapor inside the cavitation bubbles<sup>15</sup>. Secondly, the solvent vapor pressure should be lower at the sonochemical temperature since the solvent vapor inside the bubble reduces the collapse efficiency. Our group have prepared amorphous Ni and  $\text{Fe}_2\text{O}_3$  and also showed that one could control the particle size of the amorphous iron by varying the precursor,  $\text{Fe}(\text{CO})_5$  concentration in decalin<sup>16-18</sup>. The present study is a part of our ongoing project on the synthesis and characterization of nanosized amorphous metals and alloy particles.

## EXPERIMENTAL

Iron pentacarbonyl (Adrich) was used without further purification. Nickel carbonyl (Pfaltz and Bauer, Inc) was distilled prior to use. Pentane (Fluka) and decalin (Sigma) were dried with sodium metal or 4Å molecular sieve and stored inside the glove box. The sonochemical solution was degassed by purging with high pure argon ( $< 10\text{ppm O}_2$ ). FeNi alloy was prepared by ultrasonic irradiation of the solution of  $\text{Fe}(\text{CO})_5$  and  $\text{Ni}(\text{CO})_4$  in decalin at 273 K, under 1 to 1.5 atm of argon with a high intensity ultrasonic probe (Sonics & Materials, Model VC-600, 0.5 inch, Ti horn, 20kHz,  $100\text{W}/\text{cm}^2$ ). After three hours of irradiation a black powder was obtained which was centrifuged, and washed with dry pentane inside the glove box. Centrifuging and washing were repeated for at least five times. The composition of the FeNi alloy can be varied by changing the molar concentration of the precursors.

Powder X-ray diffractograms were recorded on Rigaku X-ray diffractometer (Cu K $\alpha$  radiation,  $\lambda = 1.5418\text{\AA}$ ). Scanning electron micrographs and energy dispersive analysis of X-ray spectrum (EDX) was carried out on JEOL-JSM-840 electron microscope. Transmission micrographs were obtained from JEOL-JEM100SX electron microscope. Magnetic data were collected on a Quantum Design MPMS SQUID magnetometer. Surface area (BET method) was measured on Micromeritics surface area analyzer. Mössbauer spectroscopic studies were carried out at 300 K using a conventional constant acceleration spectrometer with 50 mCi  $^{57}\text{Co}:\text{Rh}$  source. All sample preparation and transfers for these measurements were done inside the glove box.

## RESULTS AND DISCUSSION

Alloy compositions were determined by elemental and EDX analyses. Since the atomic no. of Ni and Fe are similar, the ratio of the X-ray intensities from these elements can be approximated to the alloy composition. Further these particles are much smaller than the free path for X-ray transmission through solids, i.e., 100 nm, so the X-ray intensities need not be corrected for absorption and fluorescence effects. The elemental analysis shows the amorphous alloys powder has 95% metal by weight, with trace amounts of carbon (3%) and oxygen (2%), which are presumably from the decomposition of alkane solvents or the adsorbed CO during ultrasonication. The amorphous nature of the alloy particles was confirmed by various techniques such as, SEM, TEM electron microdiffraction, and X-ray diffractogram. Scanning micrographs of alloy powder show conchoidal fractures typical for non-crystalline materials<sup>10</sup>. The TEM microdiffraction of the alloy particles shows only diffuse rings which are again characteristic of amorphous materials. Fig. 1 shows the XRD pattern for the amorphous  $\text{Fe}_{20}\text{Ni}_{80}$  as well as the heated (crystallized) samples of  $\alpha$ -Fe,  $\gamma$ -Ni,  $\text{Fe}_{20}\text{Ni}_{80}$ ,  $\text{Fe}_{40}\text{Ni}_{60}$ , and  $\text{Fe}_{60}\text{Ni}_{40}$ . The X-ray diffractogram of the amorphous solid does not show any sharp diffraction patterns except for a broad peak centered around a  $2\theta$  value of  $44.6^\circ$ . After the heat treatment under argon (extra pure,  $<10\text{ ppm O}_2$ ) for 3 h (to induce crystallization) lines characteristic of  $\gamma$ -Ni (fcc phase) start appearing. One can see that even for the higher concentration of Fe in FeNi alloy ( $\text{Fe}_{60}\text{Ni}_{40}$ ), the phase is still fcc of  $\gamma$ -Ni and not bcc of  $\alpha$ -Fe. This is in accordance with the reported equilibrium structural phase diagram of FeNi binary alloys<sup>19</sup> prepared by conventional methods involving thermal treatments. Lack of any feature at  $2\theta = 65.2^\circ$  and  $82.3^\circ$  ( $\lambda = 1.5418\text{\AA}$ ) which are the expected position of bcc  $\alpha$ -Fe (200) confirms that the Fe and Ni atoms have become alloyed, rather than forming separate grains. Mössbauer spectrum (MS) for the amorphous  $\text{Fe}_{20}\text{Ni}_{80}$  alloy powder at room temperature is shown in Fig 2a. The spectrum can be visualized as the superposition of a paramagnetic singlet having isomer shift (IS) zero and a



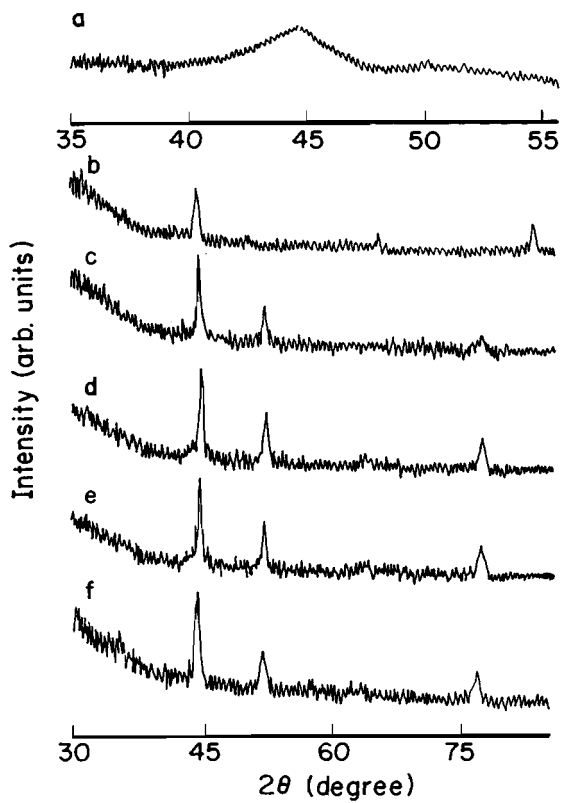


**Figure. 1.** XRD patterns for a) amorphous Fe<sub>20</sub>Ni<sub>80</sub> b) crystalline α-Fe c) crystalline γ-Ni d) crystalline Fe<sub>20</sub>Ni<sub>80</sub> e) crystalline Fe<sub>40</sub>Ni<sub>60</sub> f) crystalline Fe<sub>60</sub> Ni<sub>40</sub>.

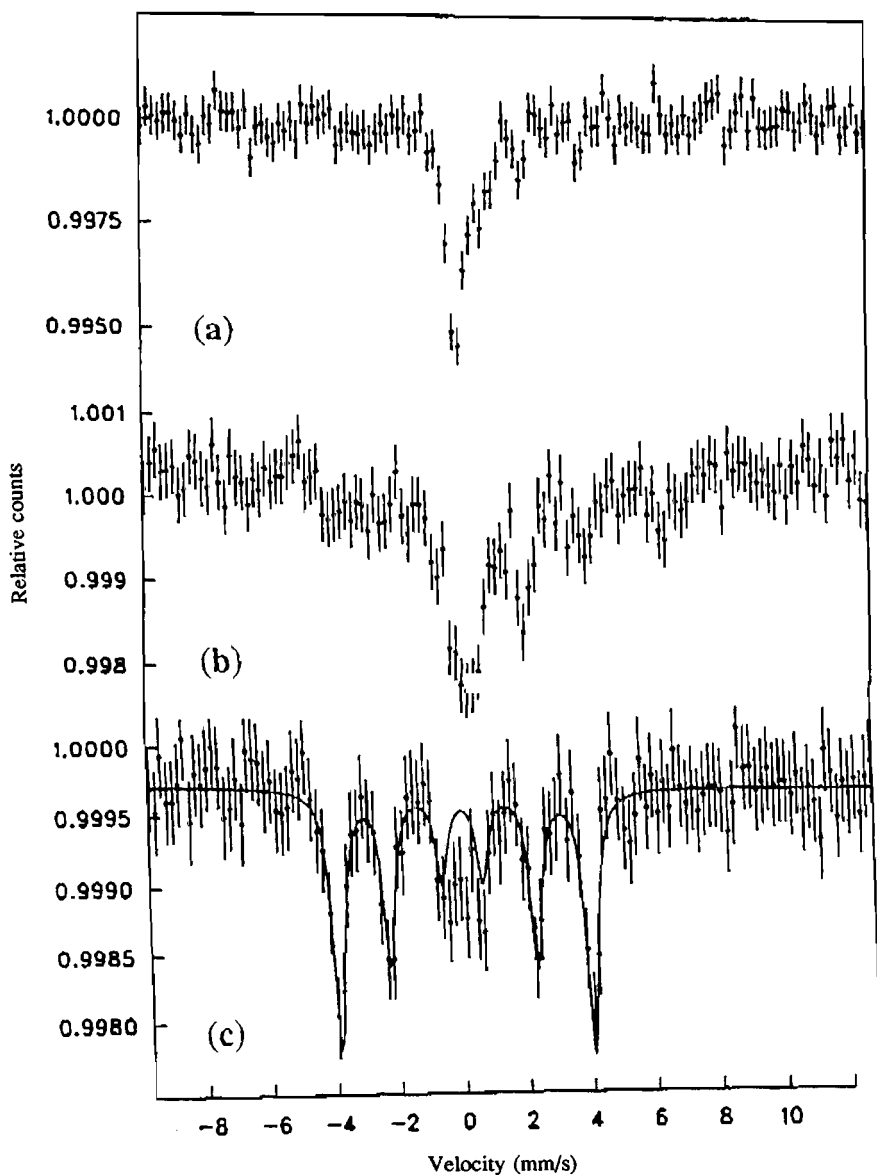


**Figure 2.** Room temperature Mössbauer spectra of amorphous  $\text{Fe}_{20}\text{Ni}_{80}$  sample. a) before heating b) after heating at 483 K for 10 h c) after heating at 693 K for 5 h

doublet (relative intensity ~35%) with an IS of -0.7 mm/s. The spectrum (Fig 4c) obtained for the amorphous sample after heating at 420° C for 5 h is completely different. A well defined sextet is observed here. It shows that the local environment for all the Fe atoms have completely changed by the annealing process and the Fe atoms are equivalent in terms of their local environment. The room temperature hyperfine parameters are: IS = 0.044(1) mm/s, effective quadruple interaction, QE = -0.06(2) mm/s and an effective magnetic hyperfine field,  $H_{\text{eff}} = 250(4)$  kOe. The existence of sextet pattern in the Mössbauer spectrum with hyperfine field value of 250(4) kOe is an additional evidence for the formation of FeNi alloy particles. This value is in the range expected for dilute concentrations of iron in Fe-Ni alloy (ca~ 265 K Oe ) and the reduction of the value (265 to 250 K Oe) can be justified if one considers that the magnetic hyperfine field of small particles may be smaller than those of corresponding bulk materials<sup>20</sup>. The magnetic hyperfine field of pure metallic iron is 330 K Oe. Fig 4b represents the MS of the amorphous sample annealed at 210° C for 10 h. It appears to be a smeared magnetic structure, reflecting the initiation of crystallization process. As in Fig. 4a, the spectral data could not be fitted here. However, one can view this spectrum as a superposition of the two spectra discussed above.

## CONCLUSION

Sonochemical decomposition of the solutions of volatile organic precursors,  $\text{Fe}(\text{CO})_5$  and  $\text{Ni}(\text{CO})_4$  in decalin at 273 K, under an argon pressure of 1 to 1.5 atm, yield amorphous nanosize FeNi alloys. The composition of alloy can be controlled by varying the initial precursor concentration in solution. We have noticed that the sonochemical efficiency for the decomposition of  $\text{Fe}(\text{CO})_5$  is less than that for  $\text{Ni}(\text{CO})_4$  and so is necessary to take an initial excess of  $\text{Fe}(\text{CO})_5$  to give a final required alloy composition. The poor efficiency of  $\text{Fe}(\text{CO})_5$  over  $\text{Ni}(\text{CO})_4$  can be traced to its very low vapor pressure when compared to  $\text{Ni}(\text{CO})_4$ . For example at 293 K, the vapor pressure of  $\text{Ni}(\text{CO})_4$  is 332 Torr where as it is only 21 Torr for  $\text{Fe}(\text{CO})_5$  at the same temperature. Further, it is well documented that  $\text{Fe}(\text{CO})_5$  on sonochemical decomposition yields a stable by product  $\text{Fe}_3(\text{CO})_{12}$  apart from metallic Fe. The surface area of the FeNi alloy particle is comparable to that of FeCo alloy prepared by Suslick et al. Our preliminary study shows that FeNi alloy particles are superparamagnetic in nature. A systematic study to understand the magnetic behavior of this alloy system is underway. We have extended our investigations to CoNi amorphous alloys and the initial results (EDX and XRD) show that particles obtained are amorphous.

## ACKNOWLEDGMENT

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# **ELECTRON ENERGY LOSS SPECTROSCOPY AS A TOOL TO PROBE THE ELECTRONIC STRUCTURE IN INTERMETALLIC ALLOYS**

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## **INTRODUCTION**

Electron energy loss spectroscopy (EELS) is a technique which provides information on the electronic structure of materials and therefore can potentially be used to probe, in an electron microscope and at high spatial resolution (i.e. down to the nanometre level), the nature of the bonding in materials and extended defects. Such studies are particularly important in intermetallic alloys which are potential candidates for high temperature structural applications. In order to maximise the information retrieved from experiments and thus provide an understanding of the bonding mechanisms (i.e. whether there is experimental evidence for some covalent character in the bond) it is important to assess first whether the theory behind the calculations of the spectra from first principles, in particular the electronic structure calculations based on the local density approximation and the single particle approach, reproduces the experimental results in bulk alloys. Second, it is important to assess whether the experimental technique is sensitive to changes in electronic structure due to, for example, alloying with ternary elements

In this work we use the spectroscopic information provided in the near edge structure (NES) of energy loss spectra which arises from the excitation of electrons from deep core levels to the first unoccupied states above the Fermi energy. This information is local (i.e. atomic species specific) and, because of the transition selection rules, angular momentum dependent: for initial *s* levels (K edges) we will observe transitions to *p* symmetry final states whereas for initial *p* levels (L<sub>23</sub> edges) transitions will occur to *s* + *d* final states. We investigate the bonding character in transition metal (TM) aluminides with the CsCl (B2) structure, FeAl, CoAl and NiAl, while assessing the validity of our calculations and then we compare the results with the bonding information provided by spectra obtained on the CuAu (L1<sub>0</sub>) TiAl structure. We also study the sensitivity of the technique to dopants (Co and Cu) in the NiAl system where we demonstrate that EELS can clearly detect changes in the density of states (DOS) and the position of the Fermi level within the DOS. Preliminary results are then shown for high spatial resolution analyses on a grain boundary in NiAl.

## **MATERIALS AND METHODS**

Alloys were prepared by arc melting high purity starting materials followed by homogenisation. Transmission electron microscopy specimens were prepared by

electropolishing 3 mm diameter disks. Energy loss spectroscopy was carried out on a Philips CM30 electron microscope equipped with a Gatan model 666 spectrometer. At the operating voltage of 100 kV an energy resolution, measured at the full width at half maximum of the no loss peak, of better than 1 eV is typically obtained. High resolution analyses were carried out on a dedicated scanning transmission electron microscope (Vacuum Generator HB501) with a probe of about 1 nm.

Theoretical calculations were performed with the linear muffin tin orbital (LMTO) method and the local density approximation for exchange and correlation. This method was used in combination with supercell models containing up to 16 atoms to calculate the DOS. The LMTO calculations are run self consistently and the DOS obtained are combined with the matrix elements for the transitions from initial to final states as described in detail elsewhere (Botton et al., 1996a) according to the method described by Vvedensky (1992). A comparison is also made between spectra calculated for some of the B2 compounds using the Korringa-Kohn-Rostoker (KKR) method.

## RESULTS

### Stoichiometric compounds

The considerable differences between the TM  $L_{23}$  edges shown here (as an example) for Ni in the pure transition metal (Ni fcc) and in NiAl in our experiments (figure 1a) are well reproduced by our calculations, both in the shape and in the relative intensity of the edges (figure 1b). The continuum background after the edge is not reproduced in our calculations since we use a linear method of computation of the DOS and hence the bands are exhausted at high energy. This background and new edge structure are, however, well reproduced using the KKR method of calculations (figure 2) as shown in the case of the Co  $L_{23}$  edge in CoAl. This shows that the important features near the edge threshold are well reproduced by the less computationally intensive LMTO calculation. This results gives us confidence in the methodology used in our work and confirms that both the local density approximation and the single particle approach describe the spectra with reasonable accuracy. There is also reasonable agreement for the first 10-12 eV after the edge threshold for the Al  $L_{23}$  as shown for FeAl where the shoulder to the main peak at about 71-73 eV is reproduced in its energy position and intensity (figure 3) relative to the steepest edge features. A similar agreement is observed for the K edges.

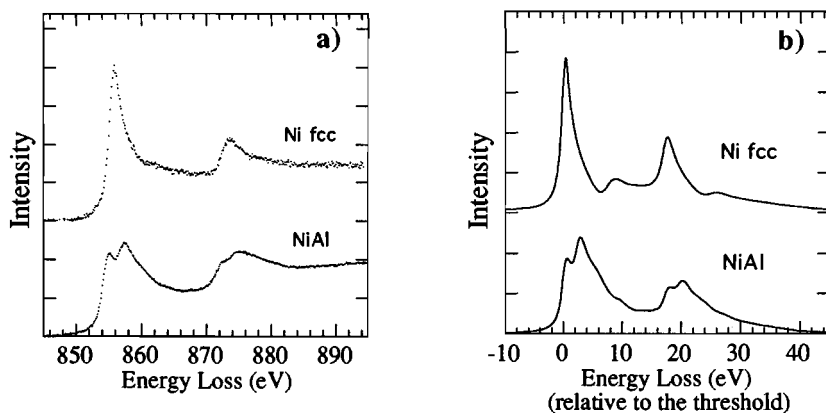


**Figure 1.** Ni  $L_{23}$  edges in NiAl and Ni (fcc) for a) EELS experiments and b) LMTO calculations.

From the analysis of the DOS combined with the interpretation of the spectral details in FeAl, CoAl and NiAl (Botton et al., 1996a) the features at the edge threshold (71-73 eV) have been shown to arise from  $d$  character being introduced at the Al sites by the strong interaction with the TM  $d$  bands and thus by the presence of "covalent" character. This interaction causes the

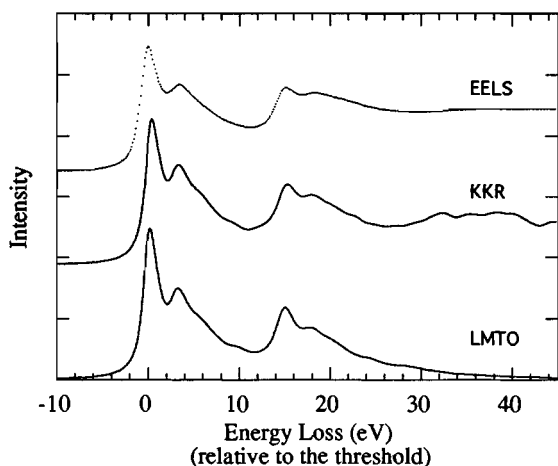


**Figure 2.** Co  $L_{23}$  edges in CoAl shown for EELS experiments (dots), LMTO and KKR calculations (lines).

reduction of Al  $s$  character in the vicinity of  $E_F$  and then the reappearance of  $s$  character at high energy in the conduction band at about 5 eV above  $E_F$  (see the peak at about 76 eV energy loss in the FeAl spectra as evidence of this effect). This interaction between the TM  $d$  and Al  $s$  bands seems less pronounced in TiAl as compared with FeAl since the intensity of the peak at 76 eV is not as strong as in FeAl as indicated by our experiments. Similar information is deduced from the Al K edges (not shown) where a shoulder in the edge is less pronounced in TiAl than in FeAl. As the features present on the K edge arise from  $p$  symmetry of final states there appears to be less interaction also between the Al- $p$  and TM- $d$  states above the Fermi level and therefore possibly in the occupied bands. In addition to these effects we report considerable anisotropy in the spectra of the Ti  $L_{23}$  edge in TiAl acquired with different momentum transfer directions. Similar effects are not detected in fcc or bcc Fe using the same acquisition technique and therefore our result on TiAl is not an artifact of the acquisition method. Because transitions occur into empty states only when the final state orbital has a component in the momentum transfer direction (e.g. Leapman and Silcox, 1979) our result indicates that the final states occupancy is not isotropic and hence that there are

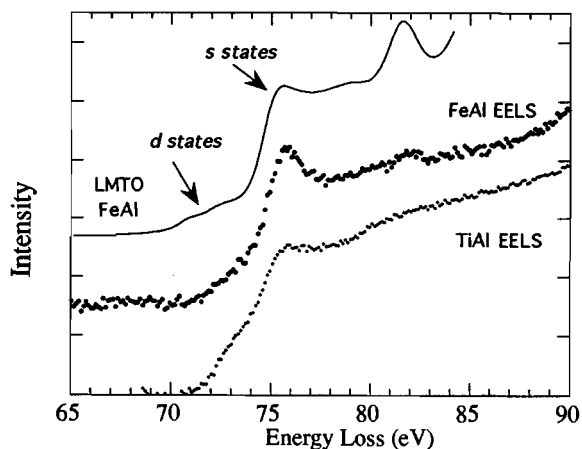


**Figure 3.** Al  $L_{23}$  edges in FeAl and TiAl (EELS experiments:dots) and LMTO calculations for FeAl (line).

some elements of directionality in the bonding character. The band decomposition of the various  $d$  orbitals  $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$ ,  $d_{z^2}$  and  $d_{x^2-y^2}$  indicates that some of the components (e.g.  $d_{x^2-y^2}$ ) are mostly below the Fermi level whereas others (e.g.  $d_{xy}$  and  $d_{yz}$ ) have their character mostly above the Fermi level and thus would contribute more significantly to the energy loss spectra. A detailed analysis showing this effect together with a simulation of the spectra will be reported later. Our preliminary results also show that our modelling approach is reasonably successful in magnetic alloys (e.g. the  $D0_3$  structure  $\text{Fe}_3\text{Al}$ ). Our preliminary results also indicate that for the Al  $L_{23}$  edge spectral features associated with splitting of the  $s$  states due to the spin polarization should be expected.

## Effect of Ternary Alloying

Since we have shown that the spectroscopic results provide considerable insight into the electronic structure variations in alloys, we can now consider the effect of ternary alloying additions in the Ni-Al based system. Here we analyse the effect of Co and Cu additions (i.e. the first neighbour TM elements to Ni) in NiAl and, because we can probe the local electronic structure at the dopant sites, the Co  $L_{23}$  and Cu  $L_{23}$  edges. Both systems  $(\text{Ni}_{.43}\text{Co}_{.07})\text{Al}_{.50}$  and  $(\text{Ni}_{.40}\text{Cu}_{.10})\text{Al}_{.50}$  form a solid solution with the B2 based structure. When Co is added, the Co  $L_{23}$  edge (figure 4) although similar to what is observed in CoAl (see figure 2) has a significantly lower first peak intensity. The NES is more similar to the Ni edge which has only slightly changed with respect to NiAl (not shown). For this edge, the differences occur again at the threshold where the first peak has only slightly increased. Because of the atomic site selectivity of EELS, we can calculate the Co  $L_{23}$  spectrum (figure 4) using the Co site DOS obtained from a supercell model where one of the Ni atoms in  $\text{Ni}_8\text{Al}_8$  has been replaced by Co ( $\text{Ni}_7\text{Co}_1\text{Al}_8$ ). The agreement is good in that the shape of the edge (the reduced intensity with respect to the secondary shoulder as compared with CoAl) and the relative energy position of the secondary shoulder of the edge with respect to the threshold agrees with experiment.

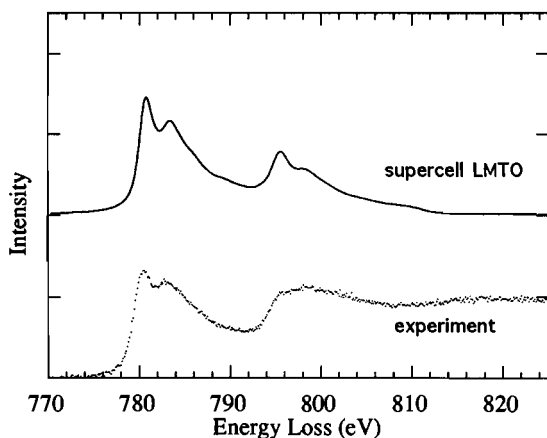


**Figure 4.** Co  $L_{23}$  edges in  $\text{Ni}_{.43}\text{Co}_{.07}\text{Al}_{.50}$  EELS (dots) and LMT0 calculation of the Co  $L_{23}$  edge in the  $\text{Ni}_7\text{Co}_1\text{Al}_8$  supercell (full line).

In a theoretical linear augmented plane wave study on the same system, Singh (1988) has concluded that a non rigid band behaviour should be expected because of the differences of the projected DOS at the Co and Ni sites which are reproduced in our self consistent supercell calculations. Because of the differences in spectra of Co and Ni, our experimental results directly support this non-rigid band behaviour noticed also directly from the spectra of the NiAl, CoAl and FeAl series (Botton et al., 1996a). Due to the differences in NES (the changes in intensity with respect to CoAl) we clearly see a band filling and charge transfer arising from the Ni atoms. Our spectra and DOS calculated from the first, second and third



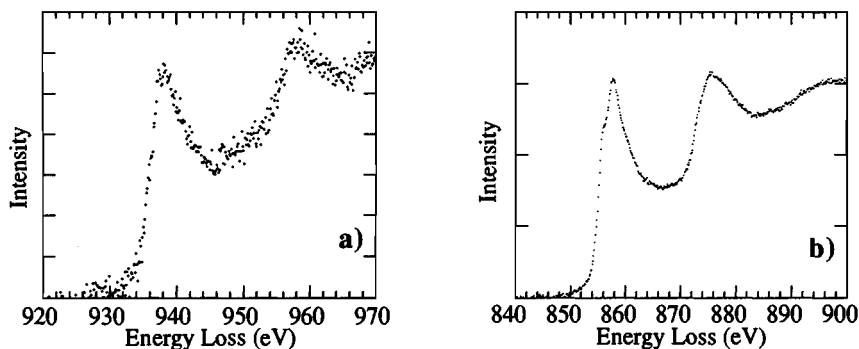


**Figure 5.** Cu L<sub>23</sub> (a) and Ni L<sub>23</sub> (b) EELS edges in the Ni<sub>4</sub>Cu<sub>1</sub>Al<sub>5</sub> alloy.

nearest Ni atoms show systematic differences in the band filling and support the charge transfer model which is enhanced for the first nearest Ni atom near the Co "impurity" as compared with the third nearest neighbour Ni atoms and in the pure NiAl compound.

A stronger charge transfer but this time from the dopant atom to Ni is seen from the (Ni<sub>40</sub>Cu<sub>10</sub>)Al<sub>50</sub> alloy spectra (figure 5 a and b). When Cu is in solid solution, the intensity of the first peak at the Ni threshold decreases significantly with respect to its form in Ni<sub>5</sub>Al<sub>5</sub> (figure 1). Looking at the L<sub>23</sub> edge of the Cu dopant, a white line appears relative to the pure Cu metal (e.g. Botton et al., 1993). This suggests that *d* holes are introduced at the dopant sites. Charge transfer from the Ni *d* bands, via hybridization, seems thus to occur upon alloying NiAl with Cu. We note also that the Cu and Ni L edges are very similar, indicative of common band behaviour in this energy range. The DOS for this system obtained with a supercell approximating the right composition (Ni<sub>7</sub>CuAl<sub>8</sub>) reproduces the common band behaviour in the energy range 1.5 eV above E<sub>F</sub> but, from the relative positions of the second peak of the Ni DOS above E<sub>F</sub> and the virtual absence of the first peak at the threshold in the Ni L<sub>23</sub> spectrum, we can deduce that the band filling is larger than predicted by the calculations assuming the Cu atoms are on the Ni sublattice. This stronger than expected band filling might be explained by recent work of Cottrell (1996) who suggested, based on energy arguments, the presence of triple defects whereby some Cu moves onto the Al sublattice and creates two vacancies on the Ni sublattice even for the alloys containing up to 50%at Al. In this case, the spectroscopic evidence suggests that there is a considerable increase in the number of valence electrons and an increase in the number of electrons filling the Ni *d* band. Because of the presence of antisite defects, the use of the KKR coherent potential approximation should therefore be used to describe more accurately the bonding mechanisms in this system.

## High Spatial Resolution Analyses

The sensitivity of EELS to electronic structure changes can be combined with the capability of performing the spectroscopic analysis with high spatial resolution in the electron microscope. The combination of these advantages and potential is demonstrated here in our preliminary results on grain boundaries in NiAl. Considerable differences are observed between spectra acquired on the grain boundary (the plane of the boundary parallel to the electron beam), using a probe of about 1 nm in size, and just a few nanometers away from the same boundary (figure 6). The effect of reduction of the first peak and the sharpness of the secondary peak cannot simply be understood by local compositional variations as the spectra from non-stoichiometric bulk alloys (Botton et al., 1996b) reveal. When Ni is in excess (Ni atoms at antisite defects) or deficient (Ni vacancies) the NES is remarkably different from the stoichiometric compound. A detailed simulation of spectra from this non-stoichiometric alloy including KKR coherent potential approximation calculations will be demonstrated elsewhere (in preparation).

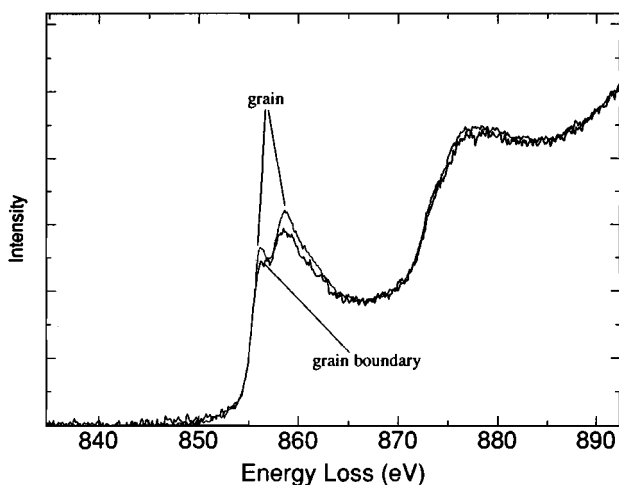


**Figure 6.** NiL<sub>23</sub> edges on a grain boundary in NiAl and a few nanometers away from the boundary (grain).

## CONCLUSIONS

Our work demonstrates that EELS and in particular the combination of this technique with first principles electronic structure calculations are very powerful methods to study the bonding character in intermetallic alloys and study the alloying effects of ternary elements on the electronic structure. Our success in modelling spectra indicates the validity of our methodology of calculating spectra using the local density approximation and the single particle approach.

We have shown that features in the spectra are associated with interaction with the TM *d* and Al *s-p* bands and thus covalent bonding. A reduced interaction strength with respect to FeAl is noted for TiAl which show anisotropy in the spectrum and thus in the bonding. For ternary alloying, we have demonstrated that the atomic species sensitivity of EELS can be put to use to study the electronic structure variation at dopant sites and the modified host lattice. For Co and Cu in NiAl we have shown that spectra indicate a region of common band behaviour and charge transfer between the Ni atoms of the host lattice and the dopants. The potential of the technique for understanding the electronic structure of defects has also been demonstrated in our preliminary results obtained with a 1 nm probe on grain boundaries of NiAl.

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# ALLOYING ASPECTS OF THE MAGNETIC GROUND STATE AND ANISOTROPY OF Fe/Cu THIN FILM OVERLAYERS

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## INTRODUCTION

The study of ultra-thin Fe thin films on Cu(001) substrate has attracted a lot of interest in the past. This is due to the abundance of interesting phenomena associated with this system. Due to the small epitaxial misfit a good layer by layer growth is expected stabilizing the film in a structure related to the fcc phase of bulk Fe which is otherwise unstable at low temperatures<sup>1</sup>. It also become a test system for magnetic measurements.

Simultaneously, computational methods have evolved to calculate reliably electronic and magnetic properties of thin film systems, including even magnetic anisotropy energies. This enables us to perform computational "experiments" to explore the various problems associated with the Fe/Cu(100) system. In particular, the Coherent Potential Approximation as combined with the Screened KKR method<sup>2</sup> can be used for such reasons. From the several problems that can be addressed this way the followings are subjects of the present paper: the magnetic ground state, the role of the spin-orbit coupling in the substrate and the effect of the intermixing between the overlayer and the substrate on the magnetic anisotropy.

## THE MAGNETIC GROUND STATE

It has been shown by several authors<sup>3-9</sup> that fcc iron films exhibit a rich magnetic structure, depending very sensitively on the atomic volume. In particular in Fe

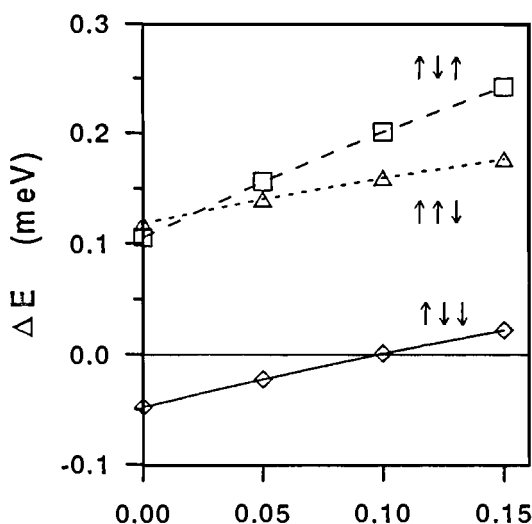


Figure 1: Energy difference between the possible antiferromagnetic states and the ferromagnetic one as the function of Au concentration in the substrate. “↑” and “↓” refer to the orientation of the magnetic moments in a layer. The substrate is assumed to be on the left hand side.

films grown on Cu(001) one distinguishes a high-moment ferromagnetic, a low-moment ferromagnetic and a low-moment antiferromagnetic phase. At the lattice constant of Cu, the system is at the edge of all these phases, therefore small differences of strain can stabilize either one. Although there are some indications, both experimental<sup>10–12</sup> and theoretical<sup>13,14</sup>, that the ground state is antiferromagnetically ordered, the actual volume dependence of the possible states and the transition between them is still not well understood. Naturally, one can think of a computer “experiment” where the lattice constant of Cu is varied, but such calculations remain rather speculative.

However, if the thin film of Fe is placed on a substrate which is an alloy of  $\text{Cu}_{1-c}\text{Au}_c$ , the continuous variation of the concentration will result in a continuous variation of the lattice constant. On the other hand, as far as effects of spin–orbit coupling are not considered, due to the very similar band structure of Cu and Au, the changes in the substrate band structure can be neglected, therefore the results can be interpreted fairly well in terms of the changes in the atomic volume. For that reason we performed scalar relativistic, spin-polarized total energy calculations for three Fe layers on  $\text{Cu}_{1-c}\text{Au}_c$  substrate ( $c < 15\%$ ) with different interlayer magnetic couplings, whereas within the planes a ferromagnetic order was considered. It should be noted, that for this concentration regime the equilibrium lattice constant of the  $\text{Cu}_{1-c}\text{Au}_c$  alloy follows Vegard’s law fairly well<sup>15</sup>. On Fig. 1 the energy difference between the possible antiferromagnetic states and the ferromagnetic state are given. It can be seen that at 10% concentration of Au the ferromagnetic ground state becomes energetically favorable. Since, as can be deduced from the data of Ref.<sup>15</sup>, this concentration belongs only to a 3.6% increase in the atomic volume with respect to the pure Cu substrate, the states corresponding to different magnetic orderings are indeed energetically rather close. Furthermore, layer relaxations close to the surface, which were not included in the present study, may bring these states even closer in energy.

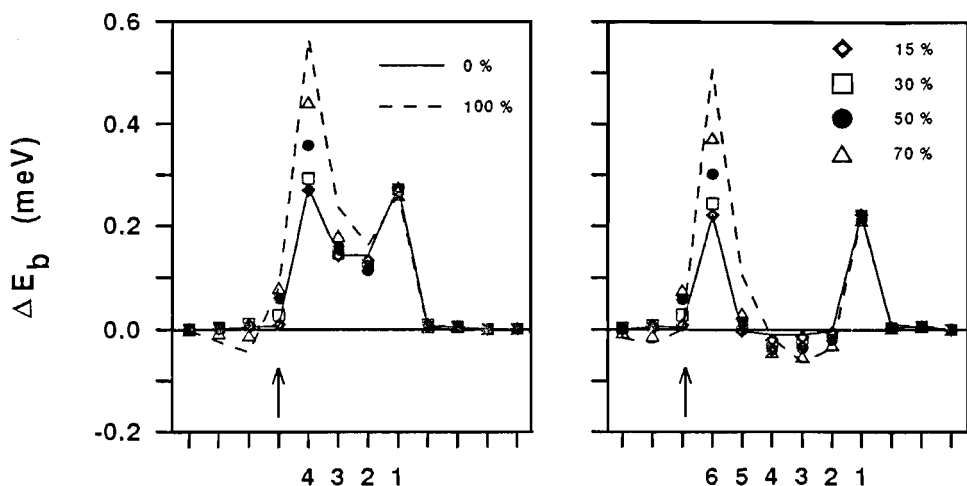


**Figure 2:** Layer-resolved band energy contributions to the MAE for Cu/Fe<sub>4</sub>/Cu (left) and Cu/Fe<sub>6</sub>/Cu (right) (001) oriented multilayers when the substrate layer marked by an arrow is alloyed by Au. The Au concentration is varied between 0 (continuous line) and 100% (broken line). Only the Fe layers are numbered.

From Fig. 1 one can also see that in the case of pure Cu substrate the  $\uparrow\downarrow\downarrow$  state is lowest in energy. As found both experimentally<sup>10</sup> and theoretically<sup>13,14,16,17</sup>, the ferromagnetic coupling between the surface and the subsurface Fe layers remains characteristic for thicker overlayers also. This feature can simply be explained by assuming that the top layers possess virtually more volume/site. As we have checked, by increasing the vacuum potential level to an unrealistically high value, squeezing therefore the orbitals on the topmost layer the antiferromagnetic coupling between the top two layers can indeed be recovered<sup>18</sup>.

## THE ROLE OF THE SPIN-ORBIT COUPLING IN THE SUBSTRATE

Ultra-thin ferromagnetic Cu/Fe<sub>*n*</sub>/Cu(001) interlayers exhibit perpendicular magnetism. While the *sp*–*d* hybridization between Fe and the Cu substrate has been found to have an essential role in this phenomenon<sup>19</sup>, the effect of the strength of spin-orbit coupling remained still an unresolved question. Since Au has a considerably larger spin-orbit coupling than Cu, the above alloying in the substrate, i.e., Cu<sub>1–*c*</sub>Au<sub>*c*</sub> offers a fine scale study of this effect. Of course, this kind of computer experiment should be confined to a constant geometry, therefore here we fixed the atomic volume at the Cu bulk value. The layer resolved band energy contributions to the magnetic anisotropy energies (MAE) for *n* = 4 and *n* = 6 are shown on Fig. 2. Clearly, the main contributions to the MAE comes from the Fe layers closest to the substrate, however, in the case of thin (*n*=4) films also the buried layers contribute remarkably. Increasing substitution of Cu by Au in a substrate layer closest to the magnetic film results in a huge enhancement of the MAE from the neighboring Fe layer increasing almost linearly with the Au concentration, while the remaining Fe layers are much less affected. Note that the contribution from the compositionally disturbed non-magnetic layer is also apparently magnified. This clearly implies that the strength of the spin-orbit coupling in the substrate displays an important factor in determining the MAE of the magnetic film. Therefore, the calculation of MAE can not correctly be performed by consid-

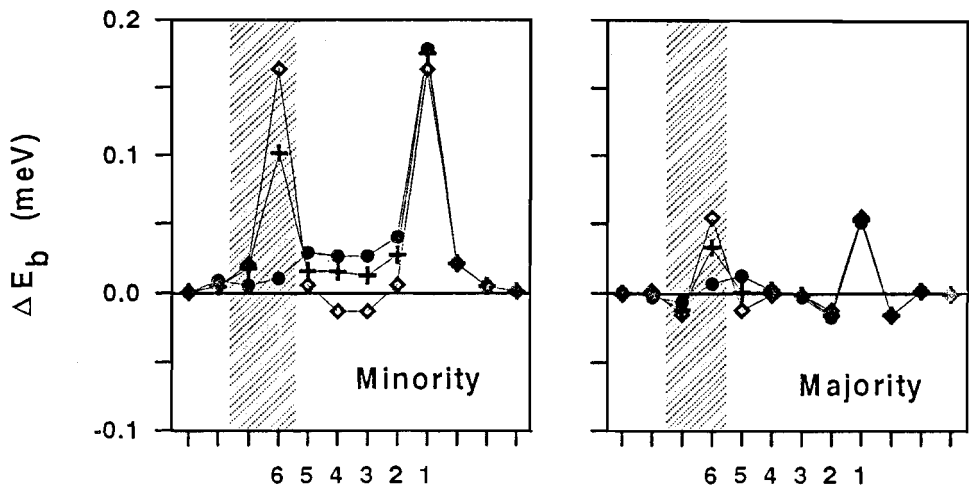


**Figure 3:** Layer-resolved band energy contributions to the MAE for Cu/Fe<sub>6</sub>/Cu (001) multilayers interdiffused at one of the Fe/Cu interfaces (shaded area). round symbols: 30 %, cross: 15 %, diamonds: 0 %. Only the Fe layers are numbered. For the interface layer of the Fe film (numbered by 1) only the contribution of the Fe component, whereas for the interface layer of the substrate (one layer to the left) only the contribution of the Cu component is displayed.

ering spin-orbit coupling in the magnetic film only as usual in techniques relying on tight-binding Hamiltonians.

## INTERMIXING EFFECTS

Up to now, most attempts made to calculate the MAE in thin films were done on ideal structures. Little is known about the effect of intermixing between the substrate and the film. Not only theoretical investigations are missing but there has been no experimental data published on the actual concentration profiles. Although Fe and Cu do not intermix at low temperatures<sup>20</sup>, effects of interdiffusion are not much studied in other systems either. Therefore calculations can be done only on simplified models of intermixing to roughly quantify its influence to the MAE. On Fig. 3 the layer- and spin-decomposed MAE's are shown for the Cu/Fe<sub>6</sub>/Cu sandwich system where intermixing is allowed between the substrate layer and the Fe layer at one interface. It is surprising to see how dramatically disorder affects the MAE, namely, at 30 % intermixing both the minority and majority contributions of Fe on layer 6 vanish (see Fig. 3). Although the subsequent two Fe layers are compositionally not affected by the intermixing, the band energy anisotropy is remarkably reduced also in these layers. Since the contribution to the MAE comes almost exclusively from the two side layers of the film, the effect of intermixing is especially pronounced.

## Acknowledgements

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# MAGNETIC DICHROISM IN VALENCE BAND X-RAY PHOTO EMISSION SPECTROSCOPY

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## INTRODUCTION

The availability of tunable synchrotron radiation of well defined polarization allowed it to refine more or less all kind of electronic spectroscopies during the last years [1]. In particular detailed information on magnetic solids [1] could be obtained by investigating the various types of spin-orbit induced magnetic dichroism. In the case of core level photo emission spectroscopy magnetic dichroism could be observed for transition metal as well as rare earth metal systems by using circularly [2], linearly [3] and even unpolarized [4] radiation in a spin-integrated as well as spin-resolved way. A corresponding theoretical description has been developed by various authors starting from an itinerant [5] or atomic description [6] of the underlying electronic structure. The linear and circular forms of magnetic dichroism in valence band (VB) photoemission has been investigated experimentally by several groups [7] in the UV regime. A proper theoretical description of these experiments on transition metal systems could be given by Feder and coworkers [8] by extending the one-step model of photo emission to the spin-polarized relativistic situation. These investigations done with polarized radiation give an extremely detailed insight into the electronic structure of the investigated material because of the various selection rules. For the X-ray regime, however, the  $\vec{k}$ -selection rule is no more present [9]. Nevertheless, as will be demonstrated below, a pronounced magnetic dichroism still occurs in that case – even for angular integrated spectra.

## EXPRESSION FOR THE XPS-PHOTO CURRENT

As has been demonstrated by various authors an expression for the photo electron current intensity  $I(E, \vec{k}, m_s; \omega, \vec{q}, \lambda)$  observed in VB-photo emission can be derived by



starting from Fermi's Golden Rule [10]:

$$I(E, \vec{k}, m_s; \omega, \vec{q}, \lambda) \propto \sum_i \left| \int d^3r \phi_{\vec{k}m_s}^{\text{final}*}(\vec{r}, E) X_{\vec{q}\lambda}(\vec{r}) \phi_i(\vec{r}, E_i) \right|^2 \delta(E - \omega - E_i). \quad (1)$$

Here the sum runs over all possible initial states  $\phi_i$  and the operator  $X_{\vec{q},\lambda}$  describes the interaction of the electrons and the radiation field with wave vector  $\vec{q}$  and polarization  $\lambda$ . In Eq. (1) it has been assumed that the detector selectively counts photo electrons with energy  $E$ , wave vector  $\vec{k}$ , and spin polarization  $m_s$ . The corresponding final state  $\phi_{\vec{k},m_s}^{\text{final}}$  is therefore identical to a time reversed LEED state  $\phi_{\vec{k}m_s}^{\text{final}} = T\phi_{-\vec{k}-m_s}^{\text{LEED}}$  with  $T = -i\sigma_y K$  the time reversal operator [11]. For the non-relativistic case Durham [12] derived an expression for  $\phi_{\vec{k}m_s}^{\text{LEED}}$  within the framework of multiple scattering theory. To allow for a investigation of the above-mentioned dichroic phenomena a corresponding fully relativistic expression has been derived recently that is applicable to spin-polarized systems [5].

To arrive at an expression for  $I(E, \vec{k}, m_s; \omega, \vec{q}, \lambda)$  one proceeds as for the non-relativistic [9] or relativistic, paramagnetic case [13] studied previously. This means that the manifold of initial states  $\phi_i$  in Eq. (1) together with the  $\delta$ -function is represented by the imaginary part of the electronic Green's function  $G^+$  [14]. Inserting the expressions for  $\phi_{\vec{k}m_s}^{\text{final}}$  and  $G^+$  into a modified form of Eq. (1) allows one to deal with spin- and angular-resolved VB photo emission in a fully relativistic way. For the XPS-regime a number of simplifications can be applied. First of all one can assume that XPS primarily probes bulk properties. This means that it is sufficient to deal with the excitation process for a representative unit cell. Second, all multiple scattering events for the final state can be ignored [9]. This single scattering approximation dramatically simplifies the evaluation of the expression for  $\phi_{\vec{k}m_s}^{\text{final}}$ . Finally arguments can be given [9] that for the XPS-regime  $\vec{k}$ -conservation does not hold any more. As a consequence the photo current  $I(E, \vec{k}, m_s; \omega, \vec{q}, \lambda)$  can be expressed by the electronic properties of a representative unit cell without any cross terms occurring. The final expression for  $I(E, \vec{k}, m_s; \omega, \vec{q}, \lambda)$  gets quite simple if it is averaged with respect to  $\vec{k}$  to simulate a powder sample or angle integrated spectrum.

If one is dealing with a randomly disordered alloy it is straightforward to perform the necessary configuration average [9]. In the case of one atom per unit cell one ends up with the following expression for the photo current

$$I(E, m_s; \omega, \vec{q}, \lambda) \propto \sum_{\alpha} x_{\alpha} \text{Im} \sum_{\substack{\Lambda \Lambda'' \\ \mu = \mu''}} C_{\Lambda}^{-m_s} C_{\Lambda''}^{-m_s} \sum_{\Lambda_1 \Lambda_2} \tau_{\Lambda_1 \Lambda_2}^{00\alpha}(E) \left[ \sum_{\Lambda'} t_{\Lambda' \Lambda}^{0,\alpha}(E') M_{\Lambda' \Lambda_1}^{\vec{q}\lambda, \alpha} \right] \left[ \sum_{\Lambda'''} t_{\Lambda''' \Lambda''}^{0,\alpha}(E') M_{\Lambda''' \Lambda_2}^{\vec{q}\lambda, \alpha} \right]^* \quad (2)$$

Here  $x_{\alpha}$  is the concentration of component  $\alpha$ ,  $t_{\Lambda\Lambda'}^{0,\alpha}$  is the single site t-matrix,  $\tau_{\Lambda\Lambda'}^{00\alpha}(E)$  is the scattering path operator and  $M_{\Lambda\Lambda'}^{\vec{q}\lambda, \alpha}$  is the matrix element with respect to  $X_{\vec{q}\lambda}$ . Finally,  $C_{\Lambda}^{m_s}$  is a Clebsch Gordon coefficient.

## RESULTS AND DISCUSSION

The approach presented above has been applied to the disordered alloy system  $\text{Co}_x\text{Pt}_{1-x}$ . Theoretical spectra for various concentrations are given in Fig. 1 for unpolarized radiation with  $\hbar\omega = 1253.6\text{eV}$ . As can be seen, these spectra agree very well

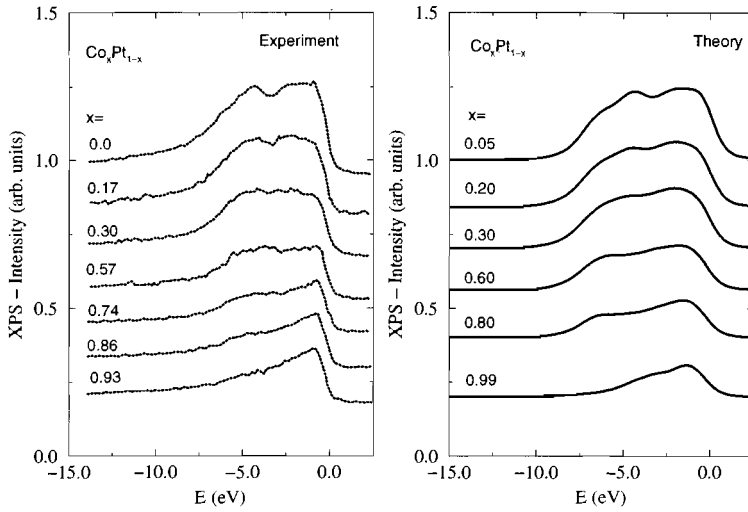


Figure 1: VB-XPS spectrum for  $\text{Co}_x\text{Pt}_{1-x}$  for unpolarized radiation and photon energy  $\hbar\omega = 1253.6$  eV. The experimental data (dashed curve) have been taken from Ref. [15].

with corresponding experimental data reported by Weller [15]. At first sight these spectra seem to be merely a concentration weighted superposition of those for pure Co and Pt. Of course, a closer look reveals that the photon absorption cross section of Pt is nearly two times larger for Pt than for Co and that there is a non-negligible variation of the component projected contributions with concentration.

For the paramagnetic case the expression for the photo current in Eq. (2) can be simplified to a concentration weighted sum over the products of the  $\kappa$ -resolved partial density of states (DOS)  $n_\alpha^\kappa(E)$  and a corresponding matrix element that smoothly varies with energy [13]. This simple interpretation of the XPS-spectra essentially also holds for the more complex spin-resolved case in the presence of spin-orbit coupling as studied here.

More detailed information on the electronic structure can be obtained by performing an XPS experiment using polarized radiation. A decomposition of the theoretical spectra in Fig. 1 results in a circular dichroism of several percent, that should be detectable in a corresponding experimental investigation – not yet done so far. An even more pronounced effect could be found if such an experiment is done in a spin-resolved way. As can be seen in Fig. 2 one can expect from the calculations a circular dichroism of 10 - 15 %. Furthermore, one observes that these spectra – if they are averaged with respect to the polarization – directly reflect the spin-resolved DOS. As can easily be deduced from the theoretical results, for  $\text{Co}_x\text{Pt}_{1-x}$  spin-polarization stems primarily from the Co-contributions in the vicinity of the Fermi energy. A way to demonstrate this also by experiment would be to vary the photon energy and to make use of a suitable Cooper minimum in the photon absorption cross section of one of the components. Such type of experiments are surely feasible, because they have already been done in the past for paramagnetic transition metal alloys.

In summary, a fully relativistic theoretical description of photo emission for magnetic solids has been presented that is based on multiple scattering theory. For the VB-XPS case a very simple expression for the photo current intensity is found that can

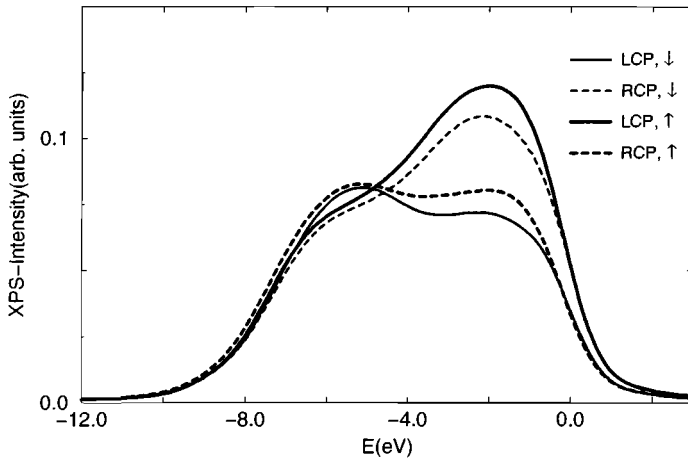


Figure 2: Theoretical spin-resolved VB-XPS spectra of  $\text{Co}_{0.6}\text{Pt}_{0.4}$  for left (LCP) and right (RCP) circularly polarized radiation and photon energy  $\hbar\omega = 1253.6$  eV.

straightforwardly applied to disordered alloys. First applications to  $\text{Co}_x\text{Pt}_{1-x}$  predict a pronounced circular dichroism – especially if the corresponding experiment is done in a spin-resolved way.

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# ELECTRONIC STRUCTURE AND BONDING IN $\text{Ti}_5\text{Si}_3$

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## INTRODUCTION

The great interest in transition-metal silicides is related to their applications in silicon technology as Schottky barriers and low-resistivity interconnections. The refractory disilicide  $\text{TiSi}_2$ , in the  $C54$  structure, is an excellent candidate for applications in integrated circuit interconnection schemes,<sup>1</sup> and is today the most commonly used silicide in the  $0.35\ \mu\text{m}$  generation of circuits.<sup>2</sup> Other crystalline titanium silicides are interesting because they are corrosion-resistive compounds. There has also been a growing attention to the preparation of amorphous alloys by mechanical alloying. Here the Ti-Si system is very interesting<sup>3</sup> due to its strong negative enthalpy of formation in the amorphous state and the fact that Si has a high diffusion rate in Ti.

The theoretical studies<sup>4-6</sup> have been focused on  $\text{TiSi}_2$ . Some attempts,<sup>7</sup> with use of high-symmetry crystal structures, have been made to understand some of the other titanium silicides. This paper deals with  $\text{Ti}_5\text{Si}_3$ . Because of the crucial interplay between structure and bonding we have studied the proposed stable low-symmetry crystal structure. This will give a better picture of the electronic structure and the bonding properties in this system. An investigation of seven members in the Ti-Si system will be presented in a future publication.<sup>8</sup>

The general understanding of the electronic structure and the bonding properties of transition-metal silicides is in terms of low-lying  $\text{Si}(3s)$  and metal- $d$  silicon- $p$  hybridization. There are two dominant contributions to the bonding in transition-metal compounds,<sup>9</sup> the decrease of the  $d$  band width and the covalent hybridization of atomic states. The former is caused by the increase in the distance between the transition-metal atoms due to the insertion of the silicon atoms, which decreases the  $d$  band broadening contribution to the stability of the lattice.

## THE BINARY SYSTEM $\text{Ti}_5\text{Si}_3$

Throughout this paper we use the *Strukturbericht* labels<sup>10</sup>  $A3$ ,  $D8_8$ ,  $A4$  for Ti,  $\text{Ti}_5\text{Si}_3$ , and Si phases, respectively. The symmetry of the  $D8_8$  structure corresponds to the  $D_{6h}^{3+}$  ( $P6_3/mcm$ ) space group. The structure is hexagonal with lattice constants<sup>11</sup>  $a=14.039$  a.u. and  $c=9.712$  a.u. The special coordinates (in fractions of the lattice constants) are

Table 1: Coordinate data for the  $D8_8$  structure.

| Atom            | Wyckoff | Coordinates   |               |               |  |
|-----------------|---------|---------------|---------------|---------------|--|
| Si              | 6g      | 0.615         | 0             | $\frac{1}{4}$ |  |
| Ti <sub>1</sub> | 4d      | $\frac{1}{3}$ | $\frac{2}{3}$ | 0             |  |
| Ti <sub>2</sub> | 6g      | 0.240         | 0             | $\frac{1}{4}$ |  |

given in Table 1. The x-coordinates for the Si atoms and the Ti<sub>2</sub> atoms are not fixed by the symmetry of the space group. The symbols in the second column are the Wyckoff notation. A complete list of all other points in the Wyckoff set is given elsewhere.<sup>10</sup> Ti<sub>1</sub> has two Ti<sub>1</sub> first, six Si second, and six Ti<sub>2</sub> third neighbors ( $d^{(1)} = 4.86 (=c/2)$ ,  $d^{(2)} = 4.99$ ,  $d^{(3)} = 5.97$  a.u.). Ti<sub>2</sub> has two Si first, three Si second, two Ti<sub>2</sub> third, four Ti<sub>2</sub> fourth, and four Ti<sub>1</sub> fifth neighbors ( $d^{(1)} = 4.73$ ,  $d^{(2)} = 5.27$ ,  $d^{(3)} = 5.83$ ,  $d^{(4)} = 5.91$ ,  $d^{(5)} = 5.97$  a.u.). Si has two Ti<sub>2</sub> first, four Ti<sub>1</sub> second, three Ti<sub>2</sub> third, and four Si fourth neighbors ( $d^{(1)} = 4.73$ ,  $d^{(2)} = 4.99$ ,  $d^{(3)} = 5.27$ ,  $d^{(4)} = 7.27$  a.u.). Distances are based on the experimental volume. Note that in  $D8_8$  the Ti-Ti nearest neighbor distance is only 89 % of the distance in  $A3$ . If we follow Harrison,<sup>12</sup> then the  $dd$  interatomic matrix elements should be about 80 % larger than in  $A3$ , due to the decrease with the fifth power of the distance.

## CALCULATION METHOD

Calculations were done with a full-potential version of the LMTO method<sup>13,14</sup> with nonoverlapping spheres. The contributions from the interstitial region were accounted for by expanding the products of Hankel functions in a series of atom-centered Hankels of three different kinetic energies. The corrected tetrahedron method<sup>15</sup> was used for Brillouin zone integration. Electronic exchange and correlation contributions to the total energy were obtained from the local-density functional<sup>16</sup> calculated by Ceperley and Alder<sup>17</sup> and parametrized by Vosko, Wilk, and Nusair.<sup>18</sup>

Three LMTO envelopes were used with the tail energies -0.01 Ry, -1 Ry and -2.3 Ry. In the first two of them,  $s, p, d$  orbitals were included and in the last one only  $s$  and  $p$  were used. It was necessary to treat the Ti  $3p$  and  $3s$  states in the semi-core state, i.e. to do a so called 2-panel calculation. The basis set for the second panel consisted of  $3s$ ,  $3p$ ,  $3d$  orbitals on the Ti sites and  $3s$ ,  $3p$  orbitals on the Si sites. The same quality  $k$ -mesh was used in all calculations to ensure maximum cancellation of numerical errors and to obtain accurate energy differences.

To be consistent, the minimum energies from the LMTO-program were used even though this underestimated the lattice constant. Murnaghan's equation of state was used to determine bulk moduli and equilibrium volumes. The energy calculations were converged within 1 mRy/atom.

In our calculations we have used experimental values<sup>11</sup> for all internal parameters in the  $D8_8$  structure. To obtain the true theoretical equilibrium structure one should also relax the structure with respect to all its internal parameters. In  $D8_8$  we have 2 coordinates and the  $c/a$  dependence of the total energy.

Table 2: Calculated and experimental values for the equilibrium volumes, bulk moduli and enthalpies of formation.

| Composition                     | Structure             | $V_0$ ((a.u.) <sup>3</sup> /atom) |                    | $B_0$ (GPa) |                    | $-\Delta H$ (mRy/atom) |                    |
|---------------------------------|-----------------------|-----------------------------------|--------------------|-------------|--------------------|------------------------|--------------------|
|                                 |                       | LMT0                              | Expt <sup>11</sup> | LMT0        | Expt <sup>19</sup> | LMT0                   | Expt <sup>20</sup> |
| Ti                              | <i>A3</i>             | 109.7                             | 119.2              | 125.3       | 105.1              | 0                      | 0                  |
| Ti <sub>5</sub> Si <sub>3</sub> | <i>D8<sub>8</sub></i> | 98.2                              | 103.6              | 157.4       | -                  | 53.2                   | 55.2               |
| Si                              | <i>A4</i>             | 133.0                             | 134.9              | 94.9        | 98.8               | 0                      | 0                  |

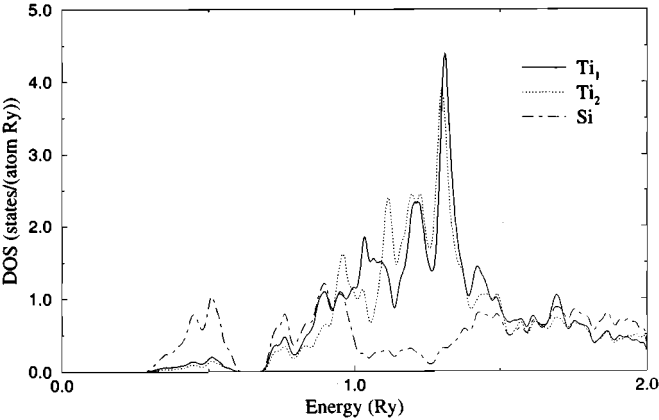


Figure 1: Decomposed DOS for *D8<sub>8</sub>*. Ti<sub>1</sub> is sited at 4d and Ti<sub>2</sub> at 6g.

### $\Delta H$ , $B_0$ AND $V_0$

Table 2 gives our calculated results for the equilibrium volume  $V_0$ , bulk modulus  $B_0$ , and enthalpy of formation  $\Delta H$ . Theoretical results refer to  $T=0$ , uncorrected for zero point motion, whereas experimental values refer to room temperature. Note that the extensive quantities  $\Delta H$  and  $V_0$  are reported per atom in the present paper, i.e., divided by the total number of atoms. As well known the LDA underestimates the volume. Comparing the bulk modulus for *A3* and *D8<sub>8</sub>* we see that the addition of Si to pure Ti has a large (26 %) effect on the bulk modulus, indicating that *p* electrons of Si have a strong effect on the bonding in this system.

### BONDING IN Ti<sub>5</sub>Si<sub>3</sub>

One way to distinguish between ionic and covalent character of the bonding in a compound is to examine the decomposed DOS. If the bonding is strongly covalent, the states from different atoms are strongly mixed and one would expect the decomposed DOS to be very similar on all sites. If the bonding is primarily ionic the decomposed DOS would be very dissimilar on sites with different atoms. To deduce the amount of hybridization in the DOS we decomposed the DOS into “site” contributions.

Figure 1 shows the decomposed DOS for *D8<sub>8</sub>*. The Fermi level is at 1.07 Ry. We see that at energies well below the Fermi level the dominant contribution is from the Si sites. The low lying state is mainly Si 3s. The small value from the Ti DOS in this region is probably due to the non-uniqueness of the site decomposition. After the gap, the Si states have mainly 3*p* character. In this region the Ti *d* states become important, and the three curves are covarying, suggesting the crucial role of hybridization in this area. Next, a quasigap opens up in the Si density, which extends to  $\sim 0.3$  Ry above

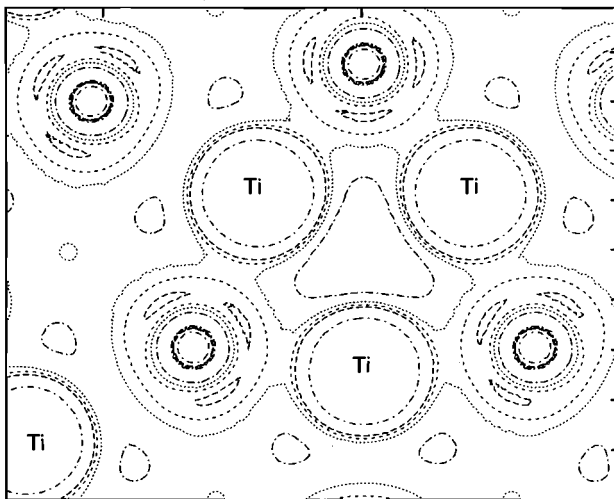


Figure 2: Charge density in the plane  $z=0.75c$ . The values are 167, 67, 57, 47, and 30 millielectrons/(a.u.)<sup>3</sup> for dot-dashed, long dashed, short dashed, dots, and dot-dashed.

$E_F$ . Above this quasigap the Si DOS again starts to covary with the Ti DOS. The Ti DOS has peaks centered at the quasigap, but there is a major overlap with the two peaks of Si  $3p$  character on each side of the quasigap. It has been shown that the quasigap in  $\text{TiSi}_2$  is due to the Ti-Si interaction.<sup>6</sup> To investigate if this is the case also in  $\text{Ti}_5\text{Si}_3$  we performed calculations of the hypothetical case of Si in  $D8_8$  without Ti atoms. These calculations do not show a quasigap in the DOS. From the disappearance of the quasigap with the removal of the Ti-Si coupling we argue that the quasigap in the Si DOS is a direct result of hybridization of the Ti  $d$  states with the Si  $sp$  band. This hybridization pushes down states in energy, which results in bonding states.

The two Ti curves do not covary in the quasigap. If the bonding was only between different atoms then the curves should covary. This indicates bonding between similar atoms. As noted above, the  $dd$  interatomic matrix elements for the  $\text{Ti}_1\text{-Ti}_1$  interaction are about 80 % larger than that in  $A3$ , supporting the idea of direct  $dd$  bonding.

Figure 2 shows the charge density in the  $[110]$  plane. In order to emphasize bonding characteristics, "valence" charge density results exclude the core and semi core contributions. The piling up of charge is not in the direction of nearest neighbors. Instead the region in between two  $\text{Ti}_2$  atoms and one Si atoms has an increased charge. From this fact it is clear that there is no two particle bonding.

## SUMMARY

We have performed full-potential calculations on  $\text{Ti}_5\text{Si}_3$  in its proposed stable crystal structure. The enthalpy of formation obtained from these calculations agrees well with the value deduced from experiment. Due to the low crystal symmetry, the possibility of a more complex bonding character arises. The charge density in this phase differs considerably from that in the hypothetical unstable structure, so two-electron bonds can be excluded in this phase. We have also showed that the opening of a quasigap in the Si DOS has its origin in the Ti-Si interaction.

## Acknowledgements

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## POLYMERIC ALLOYS: MODEL MATERIALS FOR THE UNDERSTANDING OF THE STATISTICAL THERMODYNAMICS OF MIXTURES

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### INTRODUCTION

Polymeric materials find industrial applications that are comparable to those of metals and ceramics.<sup>1</sup> In addition to the great variability via the synthesis of various monomers and the choice of the degree of polymerization ( $N$ ), alloying of polymers finds increasing attention for combining favorable materials properties.<sup>1,2</sup> But polymeric (binary) alloys (A,B) of flexible polymers with chain lengths  $N_A$ ,  $N_B$  are also most interesting for testing theoretical concepts: changing  $N_A$ ,  $N_B$  one controls the entropy of mixing, keeping intermolecular forces invariant. Variation of these control parameters thus allows stringent tests of the theories on miscibility, unmixing etc. Furthermore, the large size of the random-walk-like polymer coils (gyration radius  $R_{\text{gyr}} \approx a\sqrt{N/6}$  when  $a$  is the size of an effective statistical segment<sup>3</sup>) yields several simplifying features: (i)  $R_{\text{gyr}}$  enters as a prefactor in the correlation length  $\xi$  of concentration fluctuations, the width  $w$  of interfaces between coexisting phases near the critical point, the wavelength  $\lambda_{\text{max}}$  of maximum growth during spinodal decomposition in unstable mixtures,<sup>4,5</sup> etc. This larger length scale of cooperative phenomena allows the application of experimental techniques that would work for metallic alloys only in the immediate vicinity of the critical point.<sup>4-7</sup> (ii) Large polymer coils are objects that also move only very slowly, and thus early stages of processes such as spinodal decomposition,<sup>4-6</sup> dynamics of the formation of enrichment layers at surfaces<sup>7-9</sup>, etc. become easily accessible over a wide temperature range. (iii) Large polymer coils are rather loose, floppy objects (the monomer density  $\rho = N/V$  inside the volume taken by a coil,  $V \propto R_{\text{gyr}}^3 \propto a^3 N^{3/2}$  scales as  $\rho \propto a^{-3} N^{-1/2}$ ). In order to have a melt density of order  $a^{-3}$ ,  $N^{1/2}$  coils interpenetrate each other: in other words, every coil interacts with  $N^{1/2}$  "neighbors". This large number of neighbors is responsible for meanfield-like critical behavior as  $N \rightarrow \infty$ , and also validates<sup>4,5,10,11</sup> the linearized Cahn-Hilliard-Cook<sup>12-14</sup> theory for the initial stages of spinodal decomposition.

Using the so-called "block copolymers"<sup>5,15</sup> (a block of  $N_A$  A-monomers at one end is covalently bonded to a block of  $N_B$  B-monomers) one can also realize the analogy of order-disorder phenomena in metallic alloys with polymers: one observes transitions from the disordered melt to mesophases with various types of long range order (lamellar, hexagonal, cubic, etc.). We shall not consider these phenomena here further, however.

## MEAN-FIELD TO ISING CROSSOVER

Considering an (incompressible) polymer mixture with volume fraction  $\phi_A = \phi$  of A-monomers and volume fraction  $\phi_B = 1 - \phi$  of B monomers, the mean-field expression for the excess-free energy of mixing is given by the well-known Flory-Huggins expression<sup>3,5,16</sup>

$$f_{FH}(\phi) = N_A^{-1} \phi \ln \phi + N_B^{-1} (1 - \phi) \ln (1 - \phi) + \chi \phi (1 - \phi) \quad (1)$$

Eq. (1) follows by introducing a lattice of spacing  $a$  (either an effective segment of type A or B can take a lattice site) and writing the free energy per lattice site  $f$  (in units of  $k_B T$  where  $T$  is the absolute temperature) as a sum of the entropy of mixing and the enthalpy. In terms of nearest-neighbor pairwise interactions  $\epsilon_{AA}$ ,  $\epsilon_{BB}$ ,  $\epsilon_{AB}$ , the Flory-Huggins parameter  $\chi$  is {note that Eq. (1) neglects correlations in the occupancy of lattice sites}

$$\chi = z[\epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})/2]/k_B T \quad , \quad (2)$$

$z$  being the coordination number of the lattice. The entropy of mixing terms are down by factors  $N_A$ ,  $N_B$ , since one can take out (or insert) only chains as a whole, and not single monomers. For  $\chi > 0$  (which is the typical case here) unmixing occurs for  $T < T_{crit}$  (or  $\chi > \chi_{crit}$ , respectively;  $\phi_{crit}$  is the volume fraction at the critical point)

$$\chi_{crit} = \left( N_A^{-1/2} + N_B^{-1/2} \right)^2 / 2 \quad , \quad \phi_{crit} = \left( \sqrt{N_A / N_B} + 1 \right)^{-1} \quad (3)$$

Specializing to symmetrical mixtures ( $N_A = N_B = N$ ) for simplicity, it is easy to also find the order parameter  $\psi_{coex}$  of the unmixing transition

$$\psi_{coex} = \phi_{coex}^{(2)} - \phi_{coex}^{(1)} = \left( \phi_{coex}^{(2)} - \phi_{crit} \right) / \phi_{crit} = \sqrt{3} \left( \frac{\chi}{\chi_{crit}} - 1 \right)^{1/2} \quad , \quad \phi_{crit} = \frac{1}{2} \quad , \quad \chi_{crit} = 2 / N \quad (4)$$

For a more complete discussion of critical phenomena, we consider the scattering intensity  $S(q)$  from concentration fluctuations ( $q$  is the wavenumber of the scattering) which can be derived when one supplements Eq. (1) by a gradient-square term<sup>5,10,17</sup>

$$\begin{aligned} \frac{\Delta F}{k_B T} &= \int d^d x \left\{ f_{FH}(\phi) + \frac{a^2}{36\phi(1-\phi)} [\nabla \phi(\vec{x})]^2 \right\} \approx \\ &\approx \frac{1}{N} \int d^d x \left\{ -(\chi / \chi_{crit} - 1) \psi^2 + \frac{1}{2} \psi^4 + N a^2 [\nabla \psi(\vec{x})]^2 / 9 \right\} \quad , \end{aligned} \quad (5)$$

where we formally consider a d-dimensional system, and restrict attention to the critical region. The particular form of the gradient energy can be derived by the "random phase approximation" (RPA),<sup>10,17</sup> it is a consequence of the extended structure of the coils over a size of order  $R_{\text{gyr}}$  (rather than  $a$ , as for small molecule mixtures).

From Eq. (5) one finds<sup>5,10</sup> for  $\phi = \phi_{\text{crit}} = 1/2$  and  $\chi < \chi_{\text{crit}}$  ( $T > T_c$ )

$$S(q) = S(0)/(1+q^2\xi^2), \quad S(0) = (N/4) (1-\chi/\chi_{\text{crit}})^{-1},$$

$$\xi = (a\sqrt{2N}/6) (1-\chi/\chi_{\text{crit}})^{-1/2} \quad (6)$$

If we define critical exponents  $\beta$ ,  $\gamma$ ,  $\nu$  and amplitudes  $\hat{B}$ ,  $\hat{C}_+$ ,  $\hat{\xi}_+$  via

$$\psi = \hat{B} (\chi/\chi_{\text{crit}} - 1)^\beta, \quad S(0) = \hat{C}_+ (1-\chi/\chi_{\text{crit}})^{-\gamma}, \quad \xi = \hat{\xi}_+ (1-\chi/\chi_{\text{crit}})^{-\nu}, \quad (7)$$

we find from Eqs. (4,6) the mean-field results

$$\beta_{\text{MF}} = \nu_{\text{MF}} = \frac{1}{2}, \quad \gamma_{\text{MF}} = 1, \quad \hat{B}^{\text{MF}} = \sqrt{3}, \quad \hat{C}_+^{\text{MF}} = N/4, \quad \hat{\xi}_+^{\text{MF}} = a\sqrt{2N}/6 \quad (8)$$

The large size of  $\hat{\xi}_+^{\text{MF}}$  now is responsible for mean-field theory being reliable for large  $N$ . Invoking the Ginzburg criterion<sup>18</sup> one says mean field theory is self-consistent if the order parameter fluctuation in a correlation volume is much smaller than the order parameter itself,

$$\langle [\delta\psi(\vec{x})]^2 \rangle_{T,\xi} \ll \psi_{\text{coex}}^2 \quad (9)$$

With some algebra this condition becomes, in  $d = 3$  dimensions ( $\tau \equiv 1-\chi/\chi_{\text{crit}}$ )

$$\xi \ll R_{\text{gyr}} \sqrt{N} \quad \text{or} \quad |\tau|/Gi \gg 1, \quad (10)$$

where we have introduced the "Ginzburg number"<sup>19</sup>

$$Gi = (3/4\pi)^2 \left( \hat{B}^{\text{MF}} \right)^{-4} \left( \hat{C}_+^{\text{MF}} \right)^2 \left[ a / \left( \hat{\xi}_+^{\text{MF}} \right)^2 \right]^3 \approx 2.3/N \quad (11)$$

Only in the limit  $|\tau|/Gi \ll 1$  does one expect Ising-like critical behavior in Eq. (7) due to the universality principle of critical phenomena,<sup>20</sup>

$$\beta \approx 0.324, \quad \gamma \approx 1.24, \quad \nu \approx 0.63 \quad (12)$$

In fact, the variable  $|\tau|/Gi$  controls<sup>19</sup> the "crossover" from one "universality class"<sup>20</sup> to the other. I.e., there exists a crossover scaling description where data for various  $Gi$  (i.e., various  $N$ ) can be collapsed on a master curve. Evidence for this crossover scaling has been seen both in experiments<sup>21</sup> and in Monte Carlo simulations for the bond fluctuation model of symmetric polymer mixtures,<sup>22</sup> e.g. Fig. 1. One expects a scaling<sup>23</sup> of the form  $\psi_{\text{coex}} \sqrt{N} = \tilde{\psi}(N|\tau|)$  where the scaling function  $\tilde{\psi}$  for  $X = N|\tau| \ll 1$  reflects the Ising

behavior  $\{\tilde{\psi}(X \ll 1) \propto X^\beta$  with  $\beta \approx 0.325\}$  and for  $X \gg 1$  the mean-field behavior  $\{\tilde{\psi}(X \gg 1) \propto X^{1/2}\}$ . Interesting results of this description are power laws for the critical amplitudes in the Ising regime,<sup>23</sup>

$$\hat{B}(N) \propto N^{\beta-1/2}, \hat{C}_+(N) \propto N^{2-\gamma}, \hat{\xi}_+(N) \propto N^{1-\nu}; \tag{13}$$

some of these predictions have been verified by simulation<sup>24</sup> or experiment.<sup>25</sup>

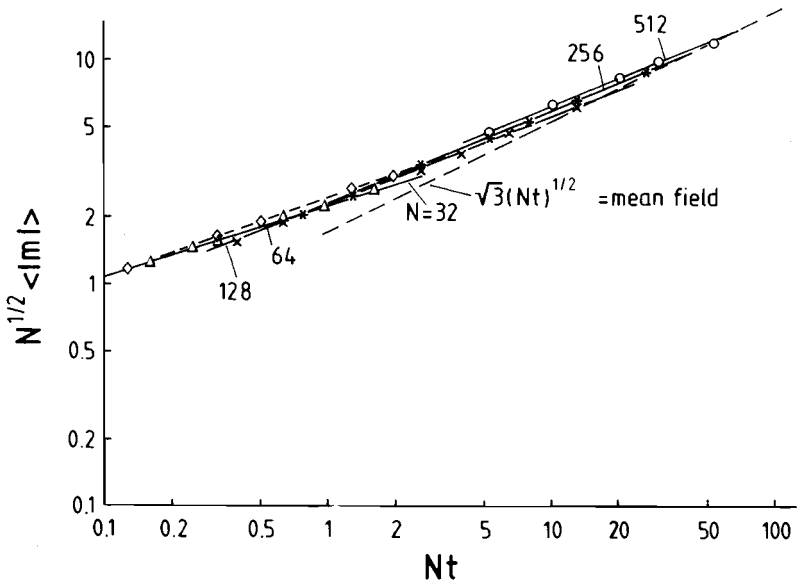


**Figure 1.** Crossover scaling plot for the order parameter  $\langle|m|\rangle = \langle|\phi_A - \phi_B| / (\phi_A + \phi_B)\rangle$  of a symmetrical polymer mixture simulated by the bond fluctuation model on the simple cubic lattice, with a concentration  $\phi_v = 0.5$  of vacant sites. Here  $N^{1/2} \langle|m|\rangle$  is plotted vs.  $Nt$ , and chain lengths from  $N = 32$  to  $N = 512$  are included. Straight lines on this log-log plot indicate effective power laws,  $\langle|m|\rangle = \hat{B}_{\text{eff}} \tau^{\beta_{\text{eff}}}$ . The broken straight line shows the mean field result {Eq. (4)} to which the data converge as  $N \rightarrow \infty$ . From Deutsch and Binder.<sup>22</sup>

### NUCLEATION AND SPINODAL DECOMPOSITION

The validity of mean field theory for  $N \rightarrow \infty$  has striking consequences for the initial stages of phase separation.<sup>10,11</sup> In a metastable state slightly inside the coexistence curve, the nucleation free energy barrier is due to spherical droplets with a radius  $R \gg \xi$ . The free energy excess of a droplet is written in terms of bulk and surface terms<sup>10,11</sup>

$$\Delta F(R) = (4\pi/3) R^3 \delta\mu_{\text{coex}} + 4\pi R^2 f_{\text{int}} \tag{14}$$

The interface free energy per unit area  $f_{\text{int}}$  is taken to be that of a planar interface between coexisting phases. Considering a solution  $\psi(z)$  that minimizes Eq. (5) subject to the boundary conditions  $\psi(z \rightarrow -\infty) = -\psi_{\text{coex}}$ ,  $\psi(z \rightarrow +\infty) = +\psi_{\text{coex}}$  one finds the excess free energy of a planar interface<sup>26</sup>

$$f_{\text{int}} \propto f_{\text{FH}}(\phi_{\text{coex}}) \xi/a \propto k_B T_c \frac{1}{3\sqrt{N}} (1 - \chi_{\text{crit}}/\chi)^{3/2} \quad (15)$$

Minimizing  $\Delta F(R)$  with respect to  $R$ , using  $\delta\mu = \delta\psi/(k_B T S(0))$  where  $\delta\psi \equiv \psi_{\text{coex}} - \psi_{\text{ms}}$  we find from Eqs. (14), (15) the free energy barrier ( $d = 3$ )

$$\frac{\Delta F^*}{k_B T_c} \propto \left[ f_{\text{int}}^3 [S(0)]^2 / \psi_{\text{coex}}^4 \right] (\delta\psi / \psi_{\text{coex}})^{-2} \propto (N|\tau|)^{1/2} (\delta\psi / \psi_{\text{coex}})^{-2} \quad (16)$$

For  $N|\tau| \gg 1$  the free energy barrier hence is very large and homogeneous nucleation is suppressed. Very close to  $T_c$ , where Eq. (10) does not hold, Eq. (15) is replaced by  $f_{\text{int}}/k_B T_c = \hat{f} (1 - \chi_{\text{crit}}/\chi)^{2\nu}$  and then all powers of  $N$  and  $\tau$  cancel out,<sup>11</sup> noting  $\hat{f} \propto N^{(2\nu - 2)}$ ,

$$\Delta F^*/k_B T_c \propto \hat{f}^3 \hat{C}_+^2 / \hat{B}^4 (\delta\psi/\psi_{\text{coex}})^{-2} \quad (17)$$

Since the prefactor in Eq. (17) is a universal constant of order unity, the barrier  $\Delta F^*/k_B T$  is large only very close to the coexistence curve, i.e. for  $\delta\psi \ll \psi_{\text{coex}}$ , while for larger  $\delta\psi$  the smallness of the barrier implies a very gradual transition from nucleation to spinodal decomposition.<sup>10,11</sup> Conversely, for  $N|\tau| \gg 1$  where Eq. (16) holds the transition is very sharp since the barrier stays large right up to the spinodal for  $N \rightarrow \infty$ .

If  $\delta\psi/\psi_{\text{coex}}$  is not small, the simple description Eq. (14) in terms of bulk and surface terms no longer holds. But one can find  $\Delta F^*$  from Eq. (5) by looking for a marginally stable non-uniform spherically symmetric solution  $\psi(\rho)$  which leads to an extremum of Eq. (5) and satisfies the boundary condition<sup>27,28</sup>  $\psi(\rho \rightarrow \infty) = \psi_{\text{ms}}$ . Near the spinodal curve  $\psi = \psi_{\text{sp}} = \psi_{\text{coex}}/\sqrt{3}$  (at this stability limit of the metastable states both  $\xi$  and  $S(0)$  diverge) one finds<sup>10,11</sup>

$$\Delta F^*/k_B T_c \propto (N|\tau|)^{1/2} [(\psi_{\text{ms}} - \psi_{\text{sp}})/\psi_{\text{coex}}]^{3/2} \quad (18)$$

The ultimate limit of metastability is reached in reality when  $\Delta F^*/k_B T_c$  is of order unity. Thus the width over which the spinodal singularities are rounded can be estimated from  $\Delta F^*/k_B T_c \propto 1$  as

$$(\psi_{\text{ms}} - \psi_{\text{sp}})/\psi_{\text{coex}} \propto (N|\tau|)^{-1/3} \quad (19)$$

A similar treatment applies for the unstable regime of the phase diagram ( $\psi < \psi_{\text{sp}}$ ), where the mixture decays via spinodal decomposition.<sup>4-6</sup> For the linearized theory of spinodal decomposition to hold, we must require that the mean square amplitude of the growing concentration waves is small in comparison with the distance from the spinodal curve,

$$\left\langle [\delta\psi(\vec{x}, t)]^2 \right\rangle_{T, L=\lambda_c} \ll [\psi - \psi_{\text{sp}}(\chi)]^2 \quad (20)$$

where the coarse-graining is done over a linear dimension  $L$  equal to the critical wave length  $\lambda_c = 2\pi/q_c$  {remember that in spinodal decomposition the growth rate  $R(q)$  of concentration waves behaves as  $R(q) \propto q^2(q_c^2 - q^2)$ }. Eq. (20) yields  $(q_m = q_c/\sqrt{2})$

$$[N|\tau|]^{1/2} [(\psi_{sp} - \psi)/\psi_{coex}]^{3/2} \gg \exp[2R(q_m)t] \quad , \tag{21}$$

where  $t$  is the time elapsed after the sudden quench from the initial state (in the one phase region) to the unstable state. Eq. (20) predicts that for polymers with  $N \gg 1$  and states  $\psi$  not too close to  $\psi_{sp}$  there should be a regime where the linear theory holds,<sup>10</sup> i.e. an exponential growth of fluctuations with time should be observable. This is indeed found,<sup>4-6,29</sup> and the predicted variation of the growth rate  $R(q)$  exhibiting a well-defined  $q_c$  is verified.<sup>29</sup> In fact, for small molecule systems with short range interactions (which include most metallic alloys) Eq. (20) can never be satisfied,<sup>4</sup> non-linear effects come into play during the early stages of unmixing already, and the linearized theory<sup>12-14</sup> is not a quantitatively accurate description. Thus polymer mixtures<sup>4-6,10,29</sup> so far provide perhaps the most beautiful illustration of the concept of spinodal decomposition, as envisaged by Cahn.<sup>12-14</sup>

### ASYMMETRICAL MIXTURES AND SOLUTIONS

As Eq. (3) shows, the critical composition  $\phi_{crit}$  can be controlled by the asymmetry of chain lengths. Particularly interesting is the limit  $N_A = N, N_B = 1$  (which physically is realized by polymer solutions,  $B$  representing a solvent of variable quality). Checking the deviations from the mean field predictions, Eq. (3), further contributes to the understanding of the statistical mechanics of mixtures.

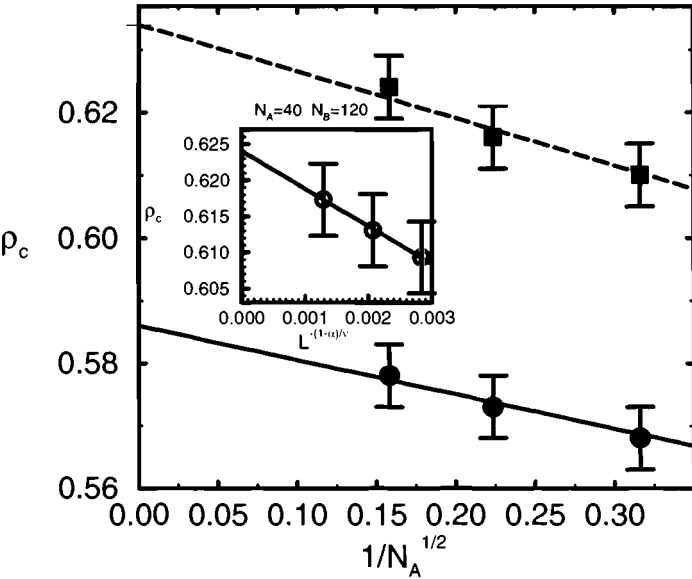


**Figure 2.** Critical volume fraction  $\phi_{crit}$  plotted vs.  $N_A^{-1/2}$  for  $k = N_B/N_A = 2$  (circles) and  $k = 3$  (squares). The inset illustrates the extrapolation of the simulation data to the thermodynamic limit according to mixed field finite size scaling<sup>31</sup> for  $N_A = 40$  and  $N_B = 120$ . From Müller and Binder.<sup>31</sup>

Recently efficient techniques were developed to simulate<sup>30</sup> and analyze<sup>31</sup> polymer mixtures with  $N_B/N_A = k$ ,  $k > 1$  being an integer. Going beyond meanfield theory, an essential point of asymmetric systems is the coupling<sup>31</sup> between fluctuations of the volume fraction  $\phi$  and the energy density  $u$ . This coupling may obscure the analysis of critical behavior in terms of the power laws, Eq. (7). However, it turns out that one can construct suitable linear combinations of  $\phi$  and  $u$  that play the rôle of the order parameter  $\psi$  and energy density  $\varepsilon$  in the symmetrical mixture,<sup>31</sup>

$$\psi = M - M_{\text{crit}}, M = (\phi - su)/(1 - sr), \varepsilon = (u - r\phi)/(1 - sr) \quad , \quad (22)$$

where the "field mixing parameters" can be extracted from a finite size scaling analysis.<sup>31</sup> Here  $r$  is identifiable as the limiting critical gradient of the coexistence curve in the space of variables  $\delta\mu$  and  $\chi$ . The parameter  $s$  removes the antisymmetric part from the distribution of  $\phi$  at criticality, rendering a critical distribution of  $M$  (or  $\psi$ , respectively) identical to that of symmetrical mixtures.<sup>31</sup>

With these techniques it became possible to check Eq. (3) for the bond-fluctuation model.<sup>30</sup> It was found that the critical temperature indeed scales with the expected combination  $N_{\text{eff}} = 4N_A N_B / (N_A^{1/2} + N_B^{1/2})^2$ , namely  $k_B T_c / \varepsilon = 2.15 N_{\text{eff}} + 1.35$  (where  $\varepsilon_{AB} = -\varepsilon_{AA} = -\varepsilon_{BB} = \varepsilon$  was chosen, and an effective coordination number  $z_{\text{eff}} \approx 2.5$  occurred<sup>30</sup>). Thus one finds that the coefficient in the relation  $T_c \propto N_{\text{eff}}$  is somewhat smaller than expected from Eq. (3), and in addition there is a "chain end"-correction. However, an integral equation theory<sup>32</sup> yielded  $T_c \propto \sqrt{N}$ , and the simulations<sup>22-24,30</sup> showed that this result clearly is incorrect. More recent improved versions of integral equation theories<sup>33</sup> now yield  $T_c \propto N$  as well but still the theoretical understanding of the prefactor in this relation is limited.

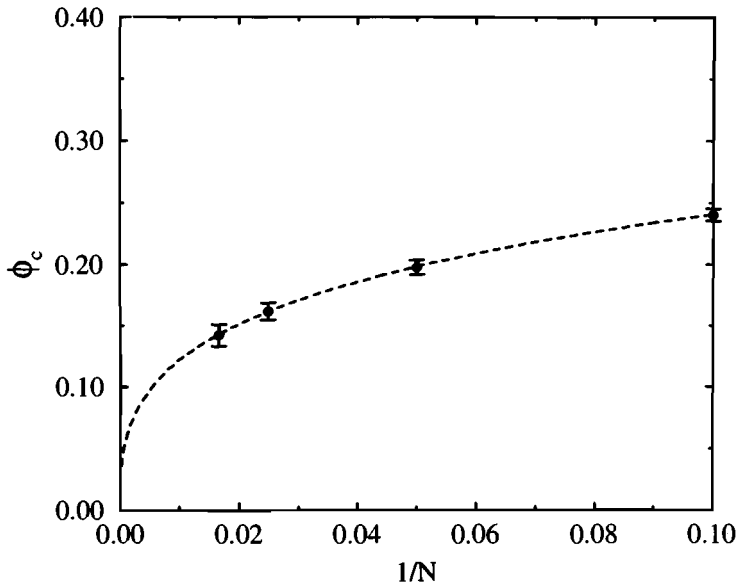


**Figure 3.** Estimates of the critical volume fraction  $\phi_{\text{crit}}$  of monomers as a function of inverse chain length. Broken curve represents a fit of the form  $\phi_{\text{crit}} = (1.1126 + 1.3 N^{0.369})^{-1}$ . From Wilding et al.<sup>34</sup>

Understanding the critical volume fraction  $\phi_{\text{crit}}$  is more subtle (Fig. 2). In accord with theoretical predictions<sup>33</sup> we find that  $\phi_{\text{crit}} = (\sqrt{N_A/N_B} + 1)^{-1}$  holds only when even the smaller chain length ( $N_A$ ) gets very large,  $N_A \rightarrow \infty$ , while for  $N_A$  large but finite corrections of order  $N_A^{-1}$  are present. A dramatic breakdown of mean field theory occurs, however, ultimately in the solution case: while the simulation data<sup>34</sup> are compatible with the relation {Eq. (3)}  $T_{\text{crit}}(\infty) - T_{\text{crit}}(N) \propto N^{-1/2}$ , the corresponding relation for the critical volume fraction  $\phi_{\text{crit}}(N) \propto N^{-1/2}$  is not confirmed: rather the data are described by  $\phi_{\text{crit}} \propto N^{-0.369}$  (Fig. 3). There is not yet any convincing theoretical explanation for this exponent<sup>35</sup> - but gratifyingly the simulation result is in excellent accord with experiments!<sup>36</sup>

## INTERFACES BETWEEN COEXISTING PHASES

Due to the smallness of the entropy of mixing, most polymer mixtures are at least partially incompatible, and blends contain A-rich and B-rich domains, separated by interfaces. The intrinsic width of these interfaces is rather broad (it varies from  $w = a/\sqrt{6\chi}$  in the "strong segregation limit"<sup>9,37</sup> to  $w = 2\xi$  in the "weak segregation limit"<sup>26</sup> near  $T_c$ . The broadness of these interfaces facilitates experimental studies of interfacial effects in polymers<sup>38</sup> (and related phenomena such as surface enrichment layers,<sup>7-9</sup> surface directed spinodal decomposition,<sup>39-42</sup> etc.). Many of these phenomena are expected to occur in small molecule mixtures as well, e.g. the unbinding  $c^f$  an A-B interface from a wall in a wetting transition,<sup>43</sup> and the theoretical concepts have been carried over from such alloys to polymers.<sup>44</sup>

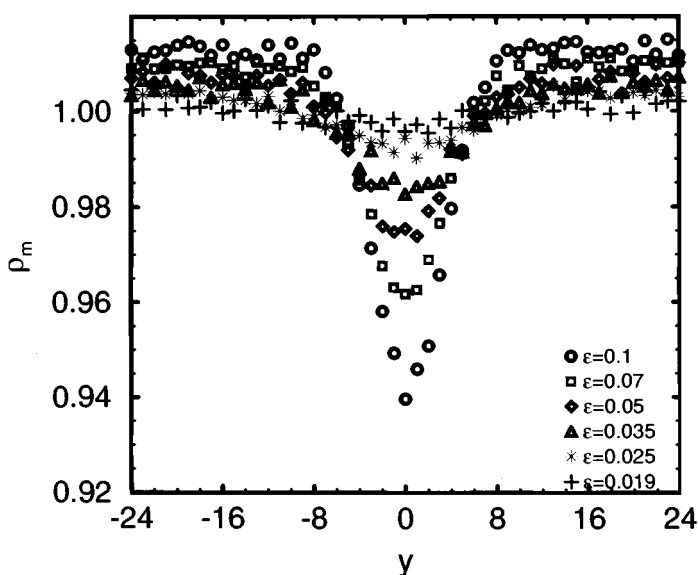


**Figure 4.** Monomer density profile  $\rho_m(y)$  {normalized such that  $\rho_m(y) \equiv 1$  if the monomers were distributed homogeneously in the simulation box} plotted vs.  $y$  at various values of  $\varepsilon/k_B T$  from  $\varepsilon/k_B T = 0.1$  (circles to  $\varepsilon/k_B T = 0.019$  (crosses). Data are for a symmetrical AB polymer mixture with  $N_A = N_B = N = 32$ , the interface occurring at  $y = 0$ . From Müller et al.<sup>45</sup>



As for polymer mixtures in the bulk,<sup>4,22-24,30,31</sup> Monte Carlo simulation of simple models provide stringent test of theoretical concepts for A-B interfaces as well.<sup>45</sup> Here we only briefly summarize the main findings:<sup>45</sup> while the temperature dependence of the interfacial free energy agrees well with the theoretical predictions, the intrinsic width is about a factor of two too large. On the other hand, the broadening of the profile due to capillary waves is smaller than expected. Nevertheless, the prediction (from simulations) that in a thin film of thickness  $D$  the A-B interface (parallel to the walls of the film) has an effective average width  $w \propto \sqrt{D}$  has been experimentally confirmed.<sup>38</sup>

Here we present only one effect in detail which also is expected to occur in metallic alloys: the enrichment of vacancies in the interfacial region (Fig. 4). For the chosen parameters, the density reduction  $\delta\rho$  in the center of the interface even is a few percent in the fully segregated limit. However,<sup>45</sup>  $\delta\rho \rightarrow 0$  as  $T \rightarrow T_c$ .

In summary, studying miscibility and unmixing in polymers gives a lot of insight into the statistical mechanics of mixtures in general and one can conveniently investigate effects that are analogously expected to occur when alloying metals, ceramics etc. Only binary mixtures and their phase separation was discussed here but these considerations clearly carry over to ternary mixtures and to some extent even to ordering phenomena.

## ACKNOWLEDGEMENTS

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# INVESTIGATION OF ORDERING KINETICS IN DEFORMED AND ANNEALED $\text{Cu}_3\text{Au}$

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## INTRODUCTION

It is obvious that knowledge about the deformation behaviour of structural materials is essential for their adequate application. In an early review Cahn<sup>1</sup> compiled several studies of solid solutions and intermetallics which investigated the correlation of order with mechanical properties. Roessler et al.<sup>2</sup> found for  $\text{Cu}_3\text{Au}$  rolled to about 60% reduction that mechanical deformation prevented ordering from proceeding quickly by domain growth. In a detailed study, Hutchinson et al.<sup>3</sup> showed that recrystallization is considerably slowed in the ordered state because of the reduced growth rate of recrystallized grains, whereas recovery is not affected within experimental accuracy. Cahn and Westmacott<sup>4</sup> in annealing  $\text{Cu}_3\text{Au}$  after rolling to more than 90% reduction observed recrystallization well below order transformation temperature  $T_i$ ; the new grains containing very coarse antiphase domains. A review of recovery and recrystallization in deformed intermetallics is given by Cahn<sup>5</sup>, who recently showed how ordered domains form at the moving grain boundary when a heavily rolled  $\text{Cu}_3\text{Au}$  sample is annealed slightly below  $T_i$ <sup>6</sup>.

Several Intermetallics, for example  $\text{Ni}_3\text{Al}$ , are ordered right up to the melting temperature showing only minor variation of order parameter with temperature. In the present paper LRO-kinetics is studied in  $\text{Cu}_3\text{Au}$ , where a  $T_i$  of about 390°C allows a considerable variation of the degree of LRO until its complete dissolution. We report on results of recrystallized material as well as samples deformed in the disordered and the ordered state. Part of this work was already presented at an earlier conference<sup>7</sup>.

## EXPERIMENTAL PROCEDURE

Samples were deformed by rolling at room temperature after disordering and quenching (40% and 80% reduction in thickness) and after ordering by a 19h annealing at 300°C (30% reduction). Completely recrystallized samples were prepared by annealing 48h at 600°C. Resistivity measurement was done by the potentiometric method in liquid  $\text{N}_2$  relative to a dummy specimen (accuracy  $\pm 3 \times 10^{-4}$ ).

The influence of mechanical deformation on LRO-kinetics was investigated during isochronal and isothermal temperature treatment.

## RESULTS AND DISCUSSION

### Completely Recrystallized Material

In Figure 1 the relative change in electrical resistivity (*residual resistometry*) during isochronal annealing ( $\Delta T=10\text{K}$ ,  $\Delta t=10\text{ min}$ ) of completely homogenised  $\text{Cu}_3\text{Au}$  after quenching from  $450^\circ\text{C}$  (disordered state) is plotted versus temperature ( $\square$ ). Changes in the LRO-parameter as calculated from measured resistivity using the Rossiter formula<sup>8</sup> are given on second axis for a comparison. In addition, the same plot with LRO-parameter in linear scaling as a main axis is shown in the insert. Up to about  $150^\circ\text{C}$  the atomic mobility is frozen and the sample remains in the disordered state. Due to the usual interpretation the decrease in resistivity in two stages at  $180^\circ\text{C}$  and  $320^\circ\text{C}$  corresponds to an increase of LRO, which is brought about by quenched-in excess and thermal vacancies, respectively. At  $360^\circ\text{C}$  the sample shows the maximum degree of LRO (about 0.6) and starts to disorder at higher temperatures until reaching the state of zero LRO at  $390^\circ\text{C}$ .

Above  $390^\circ\text{C}$  a small decrease of resistivity with increasing temperature (compare insert) signals the presence of short-range order (SRO), which is accompanied by a decrease of resistivity with decreasing degree of SRO in this system.

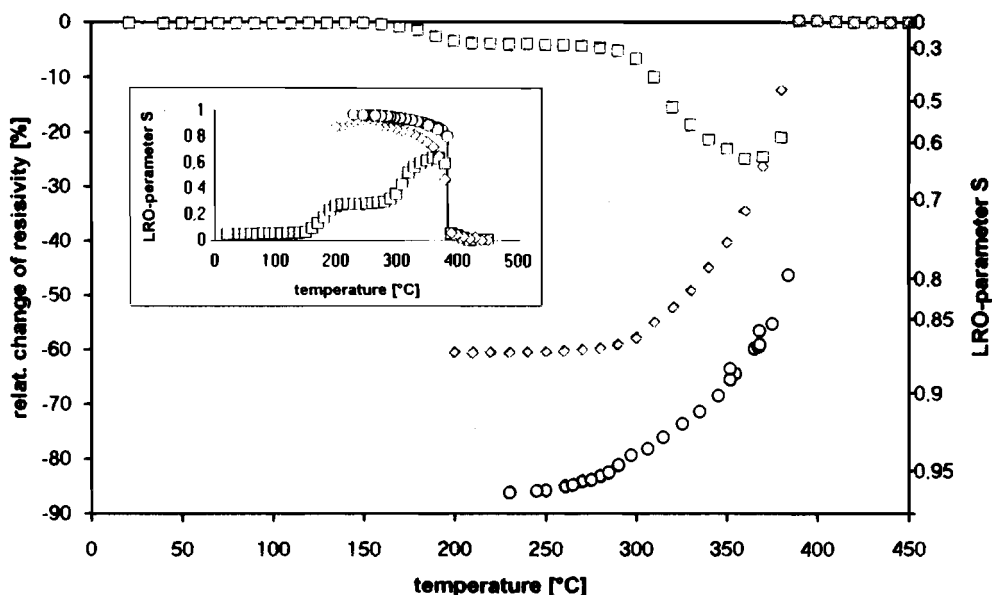


**Figure 1.** Relative change of resistivity during isochronal annealing ( $\Delta T=10\text{K}$ ,  $\Delta t=10\text{min}$ ) of completely recrystallized  $\text{Cu}_3\text{Au}$ . The LRO-parameter as calculated by Rossiter formalism<sup>8</sup> ( $A=0.5$ ) is given on second axis. ( $\square$ ) increasing, ( $\diamond$ ) decreasing temperature; ( $\circ$ ) plateau values of small step annealing procedure. Insert: Same plot with LRO-parameter as linear main scale.

That the first stage of ordering (resistivity decrease) is correlated with excess vacancies not being in thermal equilibrium can be seen from measurement during isochronally *lowering* the temperature from the disordered state ( $\diamond$ ), which shows that atomic mobility is frozen below  $280^\circ\text{C}$ .

In Figure 1 in addition to isochronal measurements plateau values of a small step annealing treatment (order-order relaxations) are given for a comparison ( $\circ$ ). These points reflect a variation of equilibrium state of LRO-parameter with temperature.

## Deformation in the Disordered State

Figure 2 gives the change of resistivity during isochronal annealing for samples cold-rolled to 40% ( $\blacktriangle$ ) and 80% ( $\bullet$ ) thickness reduction in the *disordered state* (quenched from 450°C). In contrast to the recrystallized sample no marked contribution of excess vacancies to ordering is observed for the deformed samples. The higher initial resistivity of the sample deformed to 80% results from the great number of deformation induced defects.

Whereas for the sample deformed to 40% a very small decrease of resistivity is obtained at 170°C not being visible in Figure 2 (very small number of excess vacancies) a slight *increase* results above 170°C for the sample deformed to 80%. This may be a consequence of increasing *SRO* within the disordered matrix before changes in LRO are enabled.

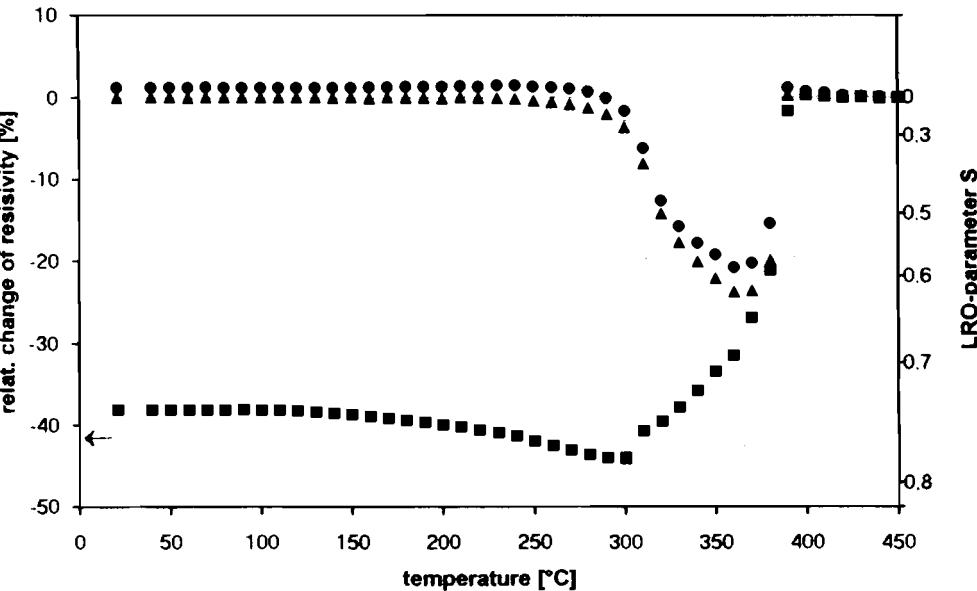


**Figure 2.** Relative change of resistivity during isochronal annealing ( $\Delta T=10K$ ,  $\Delta t=10min$ ) of deformed samples. Deformed in disordered state: 40% ( $\blacktriangle$ ) and 80% reduction ( $\bullet$ ); deformed in ordered state: 30% reduction ( $\blacksquare$ ).

## Deformation in the Ordered State

In Figure 2 the isochronal change of resistivity of an additional sample is shown ( $\blacksquare$ ), which was deformed by cold-rolling to 30% thickness reduction in the *ordered state* (pre-annealing for 19h at 300°C). The initial resistivity value after pre-annealing before deformation is given by the arrow. This resistivity increase during deformation may be due to both production of deformation induced defects and lowering of the degree of LRO by the cold work. Lowering of resistivity (increase of order) in this sample starts markedly at about 130°C although the driving force for ordering is low because of the relative high initial degree of order. Above 380°C the differences to all other samples vanish.

## Microhardness Tests

Figure 3 gives a comparison of changes in microhardness during isochronal annealing of a recrystallized sample as well as samples cold-rolled in the disordered (40% and 80%) and the ordered state (30%), respectively.

The homogenised sample shows an increase of hardness (30%) until 400°C, where a drop to the initial value is observed.

The samples deformed in the disordered state show a behaviour different for the two degrees of deformation: The sample cold-rolled to 40% at 260°C starts to decrease continuously to the completely recrystallized value, whereas the more highly deformed sample (80%) increases slightly (18%) until 390°C where a drastic decrease in hardness starts.

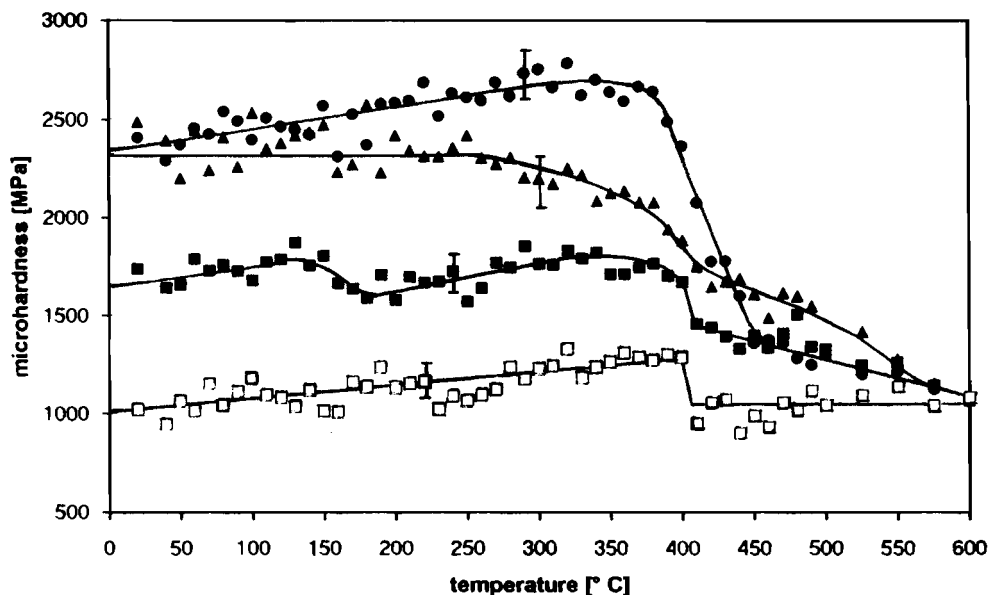


**Figure 3.** Change of microhardness during isochronal annealing ( $\Delta T=10K$ ,  $\Delta t=10min$ ) of all samples investigated. ( $\square$ ) recrystallized state, 40% ( $\triangle$ ) and 80% reduction ( $\bullet$ ) in disordered state, 30% reduction ( $\blacksquare$ ) in ordered state.

The sample deformed to 30% reduction in the ordered state shows an S-shape behaviour within the ordered region with a drop of about 30% at 400°C. The first decrease of microhardness at about 130°C seems to be correlated with the early decrease of resistivity and, therefore, may be attributed to the recovery of a great number of deformation induced excess vacancies.

From a comparison of the evolution of hardness of all samples during isochronal annealing it can be concluded that for high deformation in the disordered state and deformation in the ordered state, recovery and recrystallization is prevented up to  $T_i$ ; in the sample deformed to 40% reduction in the disordered state recovery and recrystallization processes seem to start as soon as atomic mobility is enabled (260°C).

It is observed that in all deformed samples hardness above  $T_i$  is considerably higher than the recrystallized value, which is reached for all samples at 600°C.

### Comparison of Ordering After Quenching from above $T_i$ with Order-Order Relaxations: The Influence of Antiphase Domain Growth

It is known that differences in ordering times arise between ordering after quenching from above  $T_i$  and small changes of the degree of order during small step annealing treatment below  $T_i$ , so called 'order-order' relaxations<sup>6</sup>. In Figure 4 isothermal annealing of two samples is compared. One sample always was quenched from 450°C  $> T_i$ . For the other

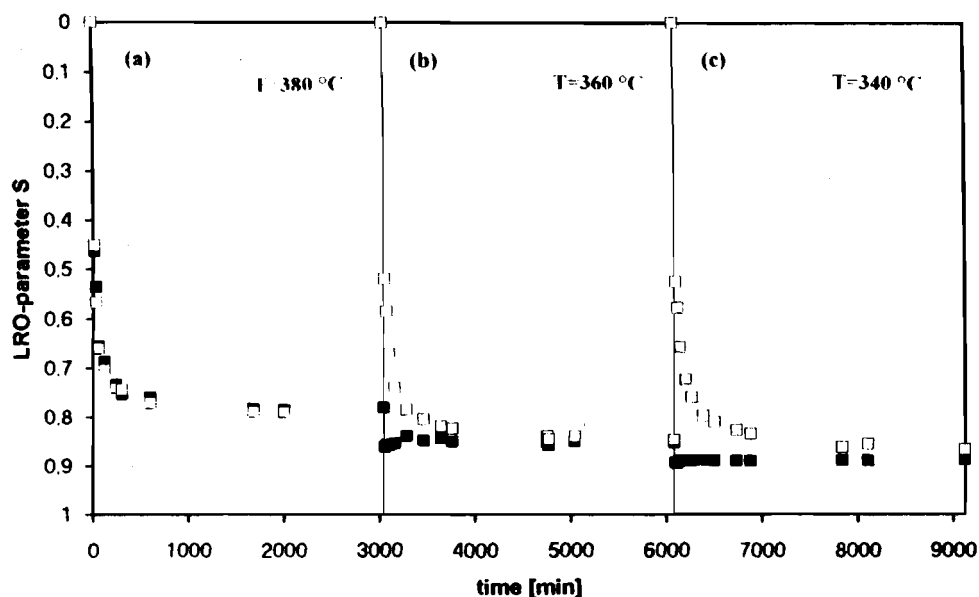


**Figure 4.** Isothermal annealing at 380°C (a), 360°C (b), 340°C (c). (□) after quenching from 450°C, (■) after quenching from 450°C (a) and subsequent annealing at 360° and 340°C (b,c), respectively.

one the final state of the first isotherm was used as a starting state for subsequent annealings. It is observed that the isotherms after quenching from temperatures above  $T_i$  show a much slower ordering behaviour than during order-order relaxations. Since it is well-known that ordering in  $\text{Cu}_3\text{Au}$  is connected with the formation and growth of antiphase domains<sup>9</sup> the differences between both curves in Figure 4b,c are ascribed to differences in the evolution of the domain structure. Therefore, an analysis of an intense study of several isothermal annealings of samples quenched from above  $T_i$  and of order-order relaxations was tried using a weighted sum of three simultaneously acting exponential processes ( $\tau_1, \tau_2, \tau_3$ ). We assume that for order-order relaxations only two processes are involved ( $\tau_1, \tau_2$ ) which we interpret as atomic jumps to nearest neighbour vacancies, decreasing (ordering) or increasing (disordering) the number of antisite atoms<sup>10</sup> *within ordered domains*. For isotherms after quenching from above  $T_i$  an additional slow process ( $\tau_3$ ) of the growth of antiphase domains has to be considered.

Figure 5 shows an Arrhenius plot of the ordering relaxation times determined in this way. Between 230° and 290°C the plot gives straight lines for all three processes yielding activation enthalpies of  $1.4 \pm 0.2$  ( $\tau_1$ ),  $1.5 \pm 0.2$  ( $\tau_2$ ) and  $1.1 \pm 0.5$  eV ( $\tau_3$ ). Values for ordering relaxation times found in the literature are scattered between 1.2 eV<sup>11</sup> and 2.1 eV<sup>12</sup> but usually are analysed using a single exponential relaxation process only. It is supposed that these activation enthalpies as in the present case correspond to different processes involved in ordering, namely formation/annihilation of antisites and domain growth, respectively. An analysis using just one exponential process probably will yield wrong activation enthalpies.

All values measured above 350°C are done for quenching from above  $T_i$ . A strong deviation from Arrhenius behaviour is observed for the fast processes. This corresponds with findings in the literature<sup>6</sup> that for ordering after quenching from above  $T_i$  a considerable slowing down of atomic jumps during ordering results, which is not observed for the case of order-order relaxations near  $T_i$  (dashed lines in Figure 5).

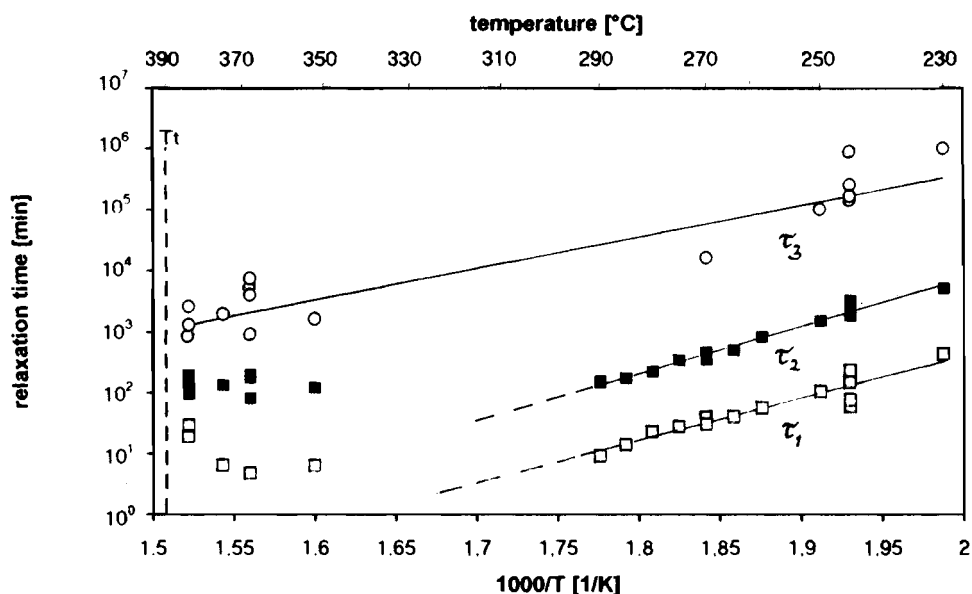


**Figure 5.** Arrhenius-plot of three relaxation times involved in total ordering process. ( $\square$ )  $\tau_1$ , ( $\blacksquare$ )  $\tau_2$ , atomic jump processes within domains; ( $\circ$ )  $\tau_3$ , change in domain size.

## Acknowledgement

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# AB INITIO INVESTIGATIONS OF PHONON ANOMALIES AND MARTENSITIC TRANSFORMATIONS

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## INTRODUCTION

Martensitic phase transformations are discussed for the last hundred years without loss of actuality. A concise definition of these structural phase transformations has been given by G.B. Olson<sup>1</sup> stating that martensite is a “diffusionless, lattice distortive, shear dominant transformation by nucleation and growth”. In this work we present *ab initio* zero temperature calculations for two model systems, Fe<sub>3</sub>Ni and CuZn close in concentration to the martensitic region. Iron-nickel is a typical representative of the ferrous alloys with fcc  $\rightarrow$  bct transition<sup>2</sup>, whereas the copper-zink alloy undergoes a transformation from the open to close packed structure<sup>3</sup>.

Our investigations focus on questions related to phase stability, magnetization (Fe<sub>3</sub>Ni) and phononic behaviour. One of our aim is the search and understanding of phonon anomalies in these systems. Lattice constants, magnetic moments and force constants have been calculated by using the full potential linearized APW method within the generalized gradient approximation (GGA)<sup>4, 5</sup>. This first principles code is only suitable for stoichiometric systems. This forces us to approximate the real disordered iron alloy by an ordered system with tetragonal or L1<sub>2</sub> symmetry.

Lattice vibrations are calculated by applying the second order perturbation theory approach of Varma and Weber<sup>6</sup>, thereby combining first principles short range force constants with the electron-phonon coupling matrix arising from a tight-binding theory.

Our resulting electronic properties agree better with experiment than known LDA calculations<sup>7</sup>. Especially for CuZn, the determination of the zero temperature ground state could be improved. Because of its small energy difference between the austenitic and martensitic phases one needs a high energy resolution. Full potential calculations combined with GGA lead to a close packed ground state for the case of CuZn which agrees with the experimental phase diagram<sup>3, 8</sup>.

## COMPUTATIONAL DETAILS

We have investigated ground state properties on a first principles basis. Total energy as well as magnetic moment (for Fe<sub>3</sub>Ni) were determined with the FLAPW method and the GGA introduced by Perdew and Wang in 1992<sup>5</sup> by employing the WIEN95 code developed by Blaha et al.<sup>4</sup>.

The magnetic Fe<sub>3</sub>Ni system was modeled in a tetragonal symmetry with 4 atoms per unit cell (see Fig. 1a). The CuZn alloy was also considered to have a tetragonal unit cell, in this case  $c/a = 1$  leads to a CsCl structure, which was shown in Fig. 1b.

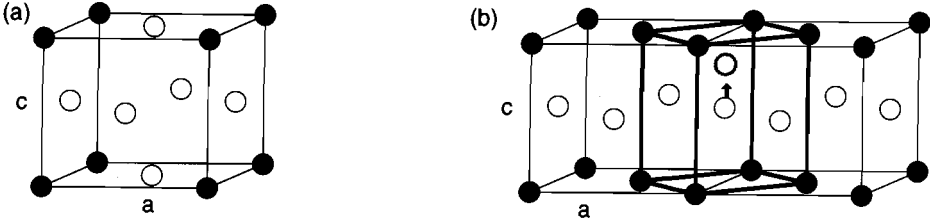


**Figure 1.** Representation of unit cells for (a) Fe<sub>3</sub>Ni and (b) CuZn. Corresponding to a tetragonal symmetry in the case of Fe<sub>3</sub>Ni (Ni atoms are marked black) and to the L1<sub>2</sub> (Cu<sub>3</sub>Au) structure in the case of  $c/a = 1$ . CuZn shows also tetragonal symmetry, whereby  $c/a = 1$  corresponds to the B2 structure (black circles represent Cu atoms). In (b) a frozen phonon in [001] direction is indicated for the Zn atom.

The existence of very small energy differences ( $\approx 0.5$  mRy) between the fct and bcc phase in CuZn, forces us to take a sufficiently large k-mesh with 2500 k-points per cell, whereas for the Fe<sub>3</sub>Ni system we may use a much smaller k-mesh (between 500 and 900) for good convergence. In order to get this high precision for the CuZn total

**Table 1.** Computational Parameters for FLAPW

| system             | $r_{MT}$ (a.u.) | k-mesh points <sup>1</sup> | $l_{max}$ <sup>2</sup> | $RK_{max}$ | $g_{max}$ <sup>3</sup> |
|--------------------|-----------------|----------------------------|------------------------|------------|------------------------|
| Fe <sub>3</sub> Ni | 2.2             | 900                        | 6                      | 8.5        | 10.5                   |
| CuZn               | 2.25            | 2500                       | 6                      | 9.5        | 10.5                   |

<sup>1</sup> tetragonal unit cell

<sup>2</sup> max. value for the multipole expansion of lattice harmonics

<sup>3</sup> max. value of G for the Fourier expansion

energy, we have to choose a plane-wave cut-off of  $RK_{max} = 9.5$ . An overview of the most important computational data is given in Table 1.

In order to determine the phonon dispersion of CuZn and Fe<sub>3</sub>Ni we made use of an expanded tight binding theory from Varma and Weber<sup>6</sup>. In the framework of a second order perturbation theory the dynamical matrix splits in two parts. The short range part can be treated by a force constant model, while the  $\mathcal{D}_2$  arising from second order perturbation theory is given by

$$\mathcal{D}_2(\kappa\alpha, \kappa'\beta|\vec{q}) = - \sum_{\vec{k}, \vec{k}' = \vec{k} + \vec{q}, \mu, \nu} \frac{f_{\vec{k}'\nu} - f_{\vec{k}\mu}}{\epsilon_{\vec{k}\mu} - \epsilon_{\vec{k}'\nu}} g_{\vec{k}\mu, \vec{k}'\nu}^{\kappa\alpha} g_{\vec{k}'\nu, \vec{k}\mu}^{\kappa'\beta}, \quad (1)$$

with the one-particle energies  $\epsilon_{\vec{k}\nu}$  and the electron-phonon matrix elements  $g_{\vec{k}\nu, \vec{k}'\mu}^{\kappa\beta}$ .<sup>9</sup> For the determination of the force constants, we made use of a frozen phonon calculation. In order to achieve this, several distortions have been done by moving one (or more) atom(s) from the equilibrium position(s). Fig. 1a gives an example for a frozen phonon in [001] direction. The curvature of these total energy curves fixes the force constants. The number of distortions taken into account depends on the crystal structure. Most of our frozen phonons are mainly influenced by short range forces (nearest and next nearest neighbours). The long range parts of the dynamical matrix is due to the electron-phonon coupling in second order perturbation.

## RESULTS

### Phase diagrams

**Fe<sub>3</sub>Ni.** In order to investigate the electronic ground state properties of Fe<sub>3</sub>Ni, we have investigated the total energy along the Bain path by using 17 c/a ratios between 0.55 and 1.15. Our results agree well with the experimental findings. A tetragonal ground state was found at c/a = 0.75 and a second very flat minimum was detected 8 mRy above the bct phase (see Fig. 1). The magnetic moment of the bct phase is 2.1  $\mu_B$  to be compared with the experimental value of 2.07  $\mu_B$ .<sup>2</sup>

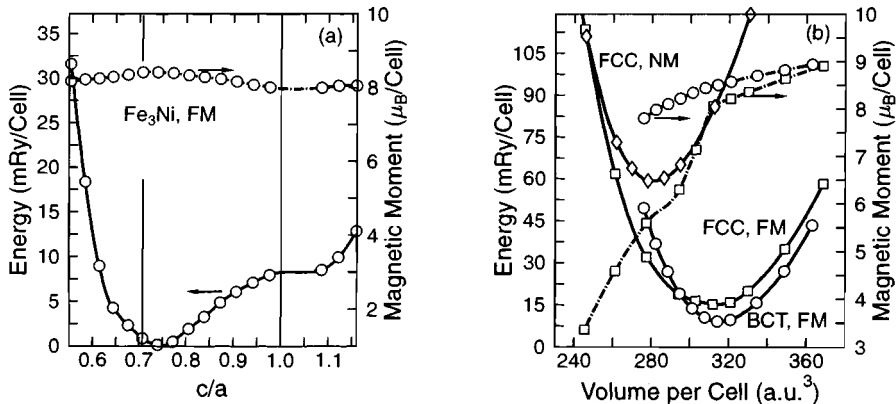


**Figure 2.** Total energy for Fe<sub>3</sub>Ni along the Bain path with  $V = \text{const}$  (a). Binding energy versus volume of the unit cell for the ferromagnetic (FM) bct (circle) and fcc (square) states. Diamonds results for the nonmagnetic (NM) fcc phase.

Additional information is taken from the binding energy curves of fcc and bct Fe<sub>3</sub>Ni (see Fig. 2b). The typical high-spin low-spin behaviour which is known from former LDA calculations, was found again for fcc Fe<sub>3</sub>Ni. The binding energy of the fcc phase is about 45 mRy lower as compared to the nonmagnetic phase corresponding to a temperature of  $\approx 1900$  K. That value is more than 4.5 times larger than the measured Curie temperature  $T_C$ . This discrepancy may be related to the fact that fcc Fe<sub>3</sub>Ni might have a noncollinear spin arrangement (whereas our calculations have been done for collinear spin arrangement) leading to a much lower value for  $T_C$ .<sup>10, 11</sup>

**CuZn.** This noble-metal alloy has a very rich phase diagram<sup>3</sup>. Many different metastable phases can be found depending on method of measuring and history of

the probe<sup>3</sup>. From the theoretical point of view, CuZn is also a complex system. Many stable states close in energy are detected in our full potential calculations. The most important curves are shown in Fig. 3a.

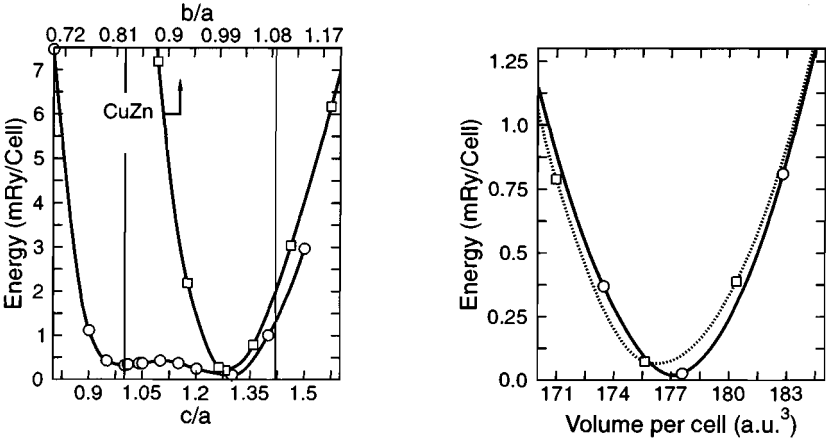


**Fig. 3:** Total energy of CuZn for different  $c/a$  ratios and constant volume (a). Binding energy versus volume curves (b) for fct (circle) and B2 (square) unit cell.

We find three phases: an fct ground state for  $c/a = 1.3$ ; an orthorhombic phase for the same  $c/a$  ratio and  $b/a = 0.99$  having 0.25 mRy higher energy, and a B2 phase at 0.5 mRy above the fct minimum. From experiments it is known that for 50at% Zn, there exists no martensitic transformation (however, at low temperatures CuZn decomposes into  $\alpha + \gamma$ ). The energy difference between all these minima is of the order of 0.5 mRy from fct to B2. Such small differences need a high energy resolution and make a full potential investigation necessary because ASA based methods<sup>7</sup> are not accurate enough.

### Phonons

**Fe<sub>3</sub>Ni.** Frozen phonon calculations combined with the determination of the electron-phonon matrix in the framework of the theory of Varma and Weber<sup>6</sup> have been carried out for the ferrous alloy. The resulting phonon dispersion for the bct phase was already presented elsewhere<sup>9</sup>. As expected, no softening or anomalous curvatures have been detected. This confirms the existence of a bct ground state for Fe<sub>3</sub>Ni.

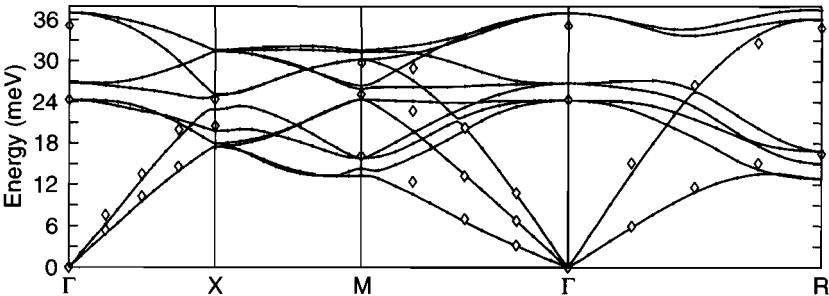


**Figure 4.** Phonon dispersion for fcc Fe<sub>3</sub>Ni (renormalized with the electron-phonon coupling). Force constants have been obtained from *ab initio* calculations. Diamonds mark experimental results<sup>12</sup>.

In opposite to this we find a soft  $TA_1$  phonon mode in  $[110]$  direction for the fcc phase (see Fig. 4). This is comparabl to the experimental findings in the case of disordered  $Fe_{65}Ni_{35}$ <sup>12</sup>. From neutron scattering experiments it is known that this softening is temperature dependent. But all involved *ab initio* methods are zero temperature algorithms. In order to understand the nature of the softening we have to pursue a different way. Using the fact that each temperature is connected with a magnetic moment and a special density of states, we take values for the temperature and volume dependent magnetic moment  $M(T,V)$  from Ginzburg-Landau functional results<sup>11</sup> and calculate the associated DOS (see Fig. 5). From this it is obvious that cooling will enhance the DOS, because the d-peak moves towards the Fermi energy. At very low temperatures the DOS decreases again. Every visible change of the density will effect

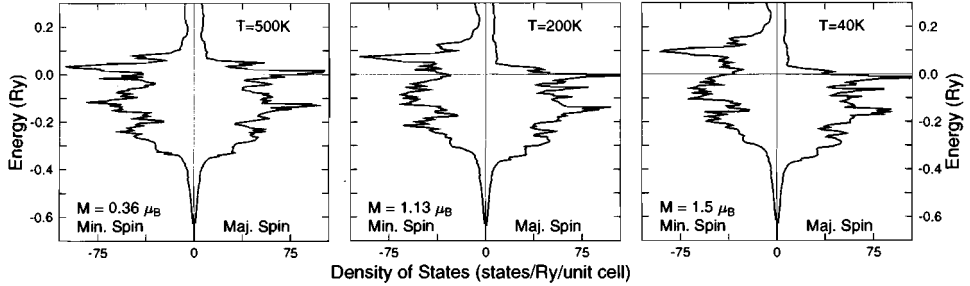


**Figure 5.** Temperature development of the electronic density of states in fcc  $Fe_3Ni$  with the temperature dependent input taken from the Ginzburg-Landau theory<sup>11</sup> (magnetic moments are given per atom).

the  $D_2$  part of the dynamical matrix. In this paper we simulate the different DOS by using  $\alpha * D_2$ , with  $0 \leq \alpha \leq 2.4$ . This simple model leads to qualitatively correct results (see Fig. 6).

Therefore the resulting  $TA_1$  mode softening in ferrous martensite can be understood

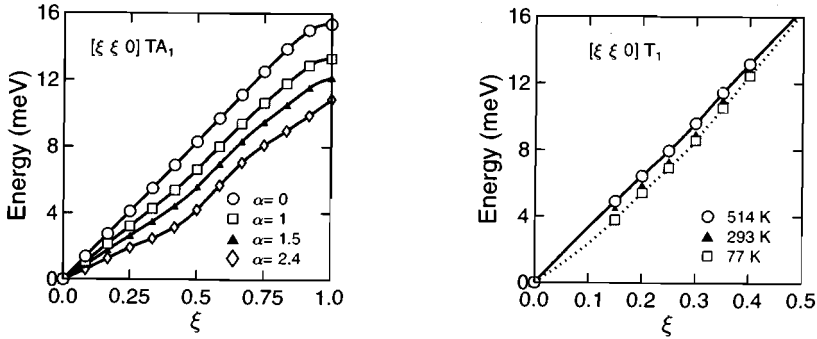


**Figure 6.**  $[110]$   $TA_1$   $Fe_3Ni$  for selected values of  $\alpha$  (a). Compared to the experimental temperature development of  $Fe_{65}Ni_{35}$ (b).

as an effect which is driven by the alternating DOS due to the temperature dependence of the magnetization. An additional aspect is, that this softening acts as a precursor of the structural phase transition, because cooling increases the phonon softening and the fcc phase loses its stability.

**CuZn.** We have investigated the phonon dispersion of the B2 phase. Our result compares well with the experimental findings marked as diamonds in Fig. 7. Similar to the fcc  $Fe_3Ni$  phase, a soft transversal mode is detected in bcc CuZn. This  $[110]$

TA<sub>2</sub> mode ( $[\bar{1}10]$  polarization) visibly depends on the influence of the electrons on the lattice vibrations (see Fig. 7). Without  $D_2$ , the stiffness of the TA<sub>1</sub> mode is enlarged. Therefore, we can conclude that this TA<sub>2</sub> mode is very sensitive to changes in the electronic structure and measures the stability of the B2 phase. This may be a hint of the temperature or stress dependence of the Cu-Zn system in the martensitic region ( $Zn \leq 42$  at%) close to the stoichiometric concentration CuZn<sup>13</sup>.

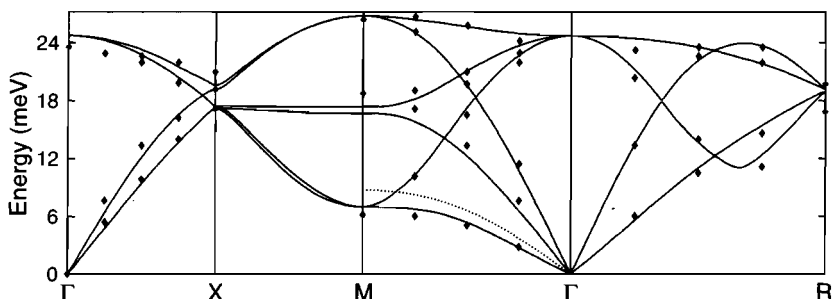


**Figure 7.** Phonon dispersion including the electron-phonon interaction for bcc CuZn. Force constants have been obtained from *ab initio* calculations. Dashed line is the phonon dispersion without the  $D_2$  contribution. Diamonds mark experimental data<sup>14</sup>.

## ACKNOWLEDGMENTS

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# INVESTIGATION OF ORDERING KINETICS IN ALLOYS BY RESIDUAL RESISTOMETRY

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## INTRODUCTION

Concentrated solid solutions usually show the effect of short-range order (SRO), this means atomic correlations which arise because of different interaction potentials between the different kinds of atom. It is known that SRO strongly influences the mechanical behaviour of materials as it induces 'planar glide' of dislocations and leads to inhomogeneous deformation. On the other hand studying the annealing behaviour after plastic deformation, changes in the microstructure of the material due to both defect recovery and changes in the degree of SRO may occur simultaneously.

If correlations between the different kinds of atom are present over long atomic distances, leading to a preference for specific sublattices, this is called long-range order (LRO). Alloys tending to LRO either can show this effect only below a certain transformation temperature well below the melting point (sequential ordering) or may remain ordered right up to the melting point (direct ordering)<sup>1</sup>. The occurrence of LRO-alloys in most cases is limited to a rather narrow range around certain stoichiometric compositions. This is especially true for directly ordering alloys and often the terminus 'Intermetallic Compound' is used to characterize the restricted solubility of these alloys.

Due to an advantageous increase of mechanical strength with temperature in a certain temperature interval Intermetallic Compounds are thought to become the most important high temperature structural materials of the future. Although the detailed origin of this surprising behaviour is still under discussion it is generally accepted that the effect is linked to the existence of LRO in these alloys. It is obvious that the stability against environmental temperature variations is of crucial importance for the technical application of structural materials. The degree of order for thermodynamic reasons is strictly dependent on temperature; therefore, there is a great need for getting knowledge about changes in the degree of order and the detailed mechanism which brings about those changes.

Changes in the atomic correlations are enabled by atomic jumps between neighbouring lattice sites. In metals and their substitutional solutions point defects are responsible for these diffusion processes. Ordering kinetics can therefore yield information about properties of the point defects which are involved in the ordering process.

Measurement of ordering kinetics of both effects LRO and SRO is difficult because of the microstructural changes being very small and often below the limit of accuracy for usual scattering experiments with X-rays or Neutrons. It is the aim of the present review to show that measuring residual electrical resistivity (*residual resistometry*) during adequate temperature treatment is a powerful tool in studying ordering kinetics and in many cases will be even the unique method which is available. The paper should enable an understanding of the experimental method and the thermal treatments involved and will present some examples of recent results on SRO and LRO systems collected in our group in Vienna.

## RELATION BETWEEN ELECTRICAL RESISTIVITY AND ORDERING

Although there have been rather early hints at the correlation between changes of resistivity and ordering<sup>2</sup> the fundamental work of Rossiter based on the pseudo-potential formalism<sup>3</sup> was of most importance for experimental research.

For SRO he obtained in relation to the completely disordered state ( $\rho_D$ ):

$$\rho_{\text{SRO}} / \rho_D = \sum_i z_i \alpha_i Y_i, \quad (1)$$

where the Warren-Cowley SRO-parameters

$$\alpha_i = 1 - (p_{AB}^i / c_B) \quad (2)$$

describe the deviation of the local atomic arrangement within the different coordination spheres ( $z_i$ ) from randomness.  $Y_i$  in eqn.(1) is an oscillating function, which depends on Fermi wave number, coordination radius and atomic potential used.

For local deviations from random atomic distribution electrical resistivity is affected just by the diffuse scattering of conduction electrons; LRO in addition will contribute to resistivity by superlattice Bragg scattering, thus changing the effective number of conduction electrons. When measuring resistivity at a low and constant temperature no phonon scattering need be considered and a rather simple formula results<sup>3</sup>:

$$\rho_{\text{LRO}} / \rho_D = (1 - S^2) / (1 - A \cdot S^2) \quad (3)$$

$S$  is the LRO-parameter and the constant  $A$  depends on the specific band structure.

Eqn(3) allows a direct determination of LRO-parameter from resistivity measurement by using the constant  $A$  as a fit parameter. Eqn(1) is of more complicated character, where besides the SRO-parameters in the different coordination spheres there enter details of the band structure ( $Y_i$ ) which influence sign and magnitude of resistivity variation with degree of SRO. However, restricting to nearest neighbours and using an adequate model for the dependence of  $\alpha$  on temperature and concentration, reliable SRO-parameters have been deduced from resistivity measurement for several solid solutions<sup>4</sup>.

A more rigorous approach for calculating the SRO-dependant residual resistivity has been attempted recently by Banhart<sup>5</sup> by entering the Kubo-Greenwood equation after calculating the scattering matrix by the embedded-cluster method (ECM) in the framework of the coherent-potential approximation. A preliminary result for Ag-15at%Al gives a very promising correspondence with experiment. Another method by Nicholson et al.<sup>6</sup> taking a large atom cluster without applying the ECM may suffer from possible influences of atomic cluster size and boundary effects.



There is a lack of calculations of alloy resistivity as a function of LRO using more advanced methods. What has already been done is applying the coherent-potential approximation to a one orbital tight-binding band<sup>7</sup>. However, a generalization to a more realistic band structure and application of other rigorous methods until now is missing.

## EXPERIMENTAL PROCEDURE AND THERMAL TREATMENT

Resistivity measurements are done on meander shaped samples by the standard potentiometric method in a stirred bath of liquid nitrogen relative to a dummy specimen<sub>3</sub>. For this procedure of *residual resistometry* the *ultra-high* measuring accuracy of  $\pm 3 \cdot 10^{-5}$  results below 300°C and of  $\pm 3 \cdot 10^{-4}$  for annealing treatments at higher temperatures.

It turned out in several investigations in recent years<sup>4</sup> that appropriate temperature treatments for resistivity measurement are done by applying isochronal and isothermal heat treatment to the samples, thus observing the establishment (ordering) or dissolution of order (disordering) with temperature and time, respectively. Figure 1 gives a schematic plot of electrical resistivity versus temperature as measured during isochronal annealing where temperature is increased in steps, each level being held constant for the same time interval. From such an investigation several features of the alloy system

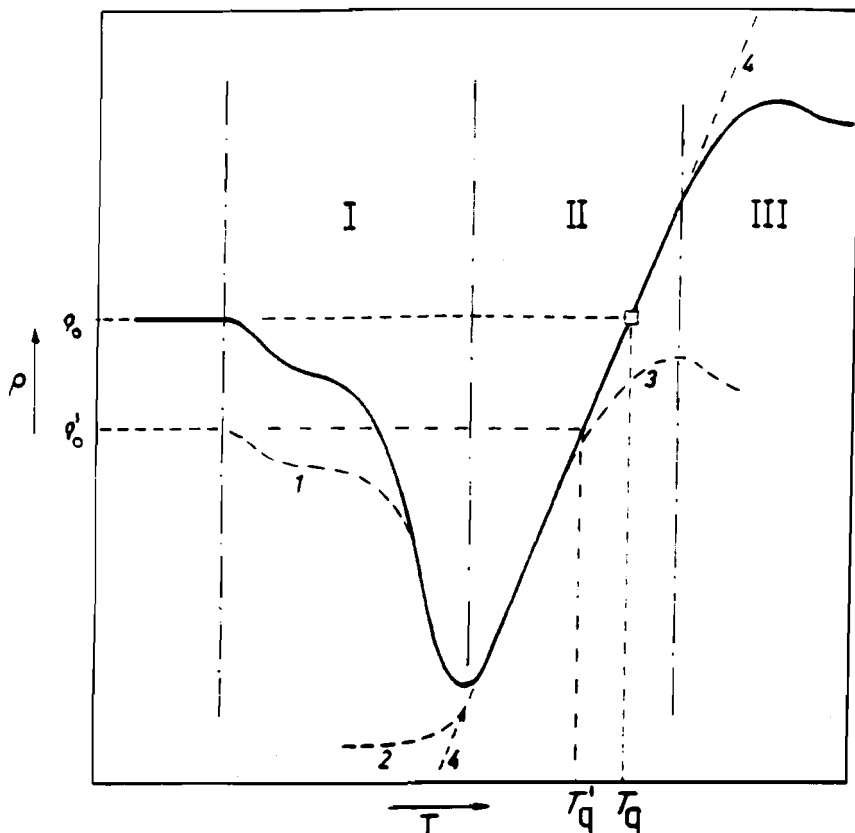


**Figure 1.** Schematic plot of residual resistivity as a function of temperature during isochronal annealing for the case of a decrease of resistivity with increasing degree of order. Range I: Increase of order due to a growing atomic mobility of surplus and thermal vacancies. Range II: 'equilibrium curve' (curve 4), resistivity change corresponds to reversible changes of order. Range III: Deviation of measured resistivity from equilibrium curve because of re-ordering during the quench. Curve 1: Influence of thermal and mechanical pre-treatment. Curve 2: Freezing of atomic mobility. Curve 3: Influence of quenching rate.

with respect to ordering kinetics can be determined:

- (i) sign and magnitude of resistivity variation with degree of order;
- (ii) the onset of atomic mobility by thermal and surplus vacancies;
- (iii) influence of thermal or mechanical pre-treatment;
- (iv) efficiency of quenching rate.

Additional isothermal treatments at neighbouring temperatures (*small step annealing*) yield plateau values of resistivity corresponding to equilibrium values at certain temperatures which reflect the order parameter in thermal equilibrium as a function of temperature ('equilibrium curve', curve 4 in Figure 1). This study can be used for an analysis of the kinetics of 'order-order' relaxations (see Figure 3 below).

It should be noted that studying states of order in thermal equilibrium as a function of temperature yields the possibility of 'measuring' the degree of order of a system in values of 'corresponding equilibrium temperature'. This way, the results of residual resistometry are independent of the detailed formalism between state of order and electrical resistivity.

## KINETICS OF SHORT-RANGE ORDERING

### Fully Recrystallized Material

Several solid solutions have been investigated in recent years with respect to SRO-kinetics by using residual resistometry and thermal treatments as described above<sup>7-12</sup>. As an example recent results on the system  $\alpha$ -AuFe are shown<sup>13,14</sup>.

In Figure 2 the relative change of resistivity during isochronal annealing ( $\Delta T=10\text{K}$ ,  $\Delta t=15\text{min}$ ) is plotted versus temperature for Au-5at%Fe (open symbols). With increasing temperature a decrease in resistivity is observed. According to the usual interpretation of SRO-isochrones the two stages of the decrease in resistivity correspond to an increase in the degree of SRO brought about by the migration of surplus vacancies (migration enthalpy  $H_m$ ) and vacancies in thermal equilibrium ( $H_m+H_f$ ), respectively. As soon as the annealing time is sufficient to enable equilibrium to be reached, a minimum is obtained. For higher temperatures the degree of SRO decreases and therefore resistivity increases with increasing temperature following an 'SRO equilibrium curve'.

Figure 3 shows a series of isothermal anneals at neighbouring temperatures (*small step annealing*) for recrystallized samples with Fe content between 5 and 20at%. The following typical features are observed:

- (i) Certain resistivity values belong to specific annealing temperatures as equilibrium values (plateau values). This can be interpreted as thermodynamic stability of SRO.
- (ii) The atomic mobility increases with Fe concentration.
- (iii) The effect of SRO on resistivity (step height) increases with concentration of Fe.

For small enough temperature steps ( $\leq 10\text{K}$ ) during small step annealing the vacancy concentration practically remains constant and corresponds to the instantaneous annealing temperature. This allows for an easy analysis of SRO-kinetics yielding SRO-relaxation times and SRO-activation enthalpies, which by usual interpretation correspond to  $H_m+H_f$ .

The decrease of resistivity in Figure 2 is caused by a contribution of surplus and thermal vacancies and therefore although *not directly* caused by changes of vacancy concentration contains information on  $H_m$  and  $H_m+H_f$  via *SRO-kinetics* (SRO-amplifier). By using a kinetic model for SRO-relaxation in which migration and formation enthalpy of vacancies enter separately together with the dislocation density as a sink density for vacancies<sup>14,15</sup>, the resistivity change during isochronal annealing in Figure 2 has been calculated (full curve) yielding satisfying correspondence with experimental results and quite reasonable dislocation density.

AuFe like CuMn is one of the well known prototype systems showing magnetic spin glass behaviour at low temperatures. It may be recognized that by the above method we are

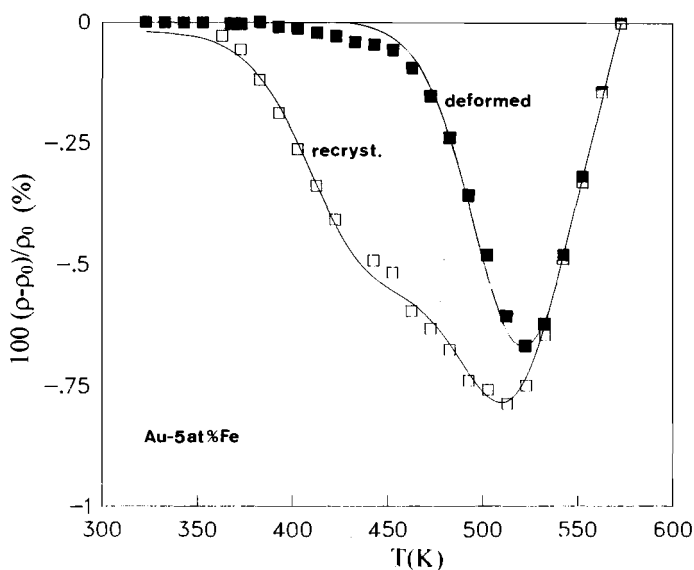


**Figure 2.** Resistivity change versus temperature for isochronal annealing ( $\Delta T=10\text{K}$ ,  $\Delta t=15\text{min}$ ) of Au-5at%Fe in the recrystallized ( $\square$ ) and deformed state ( $\blacksquare$ ) (cold-rolled to about 80% thickness reduction).

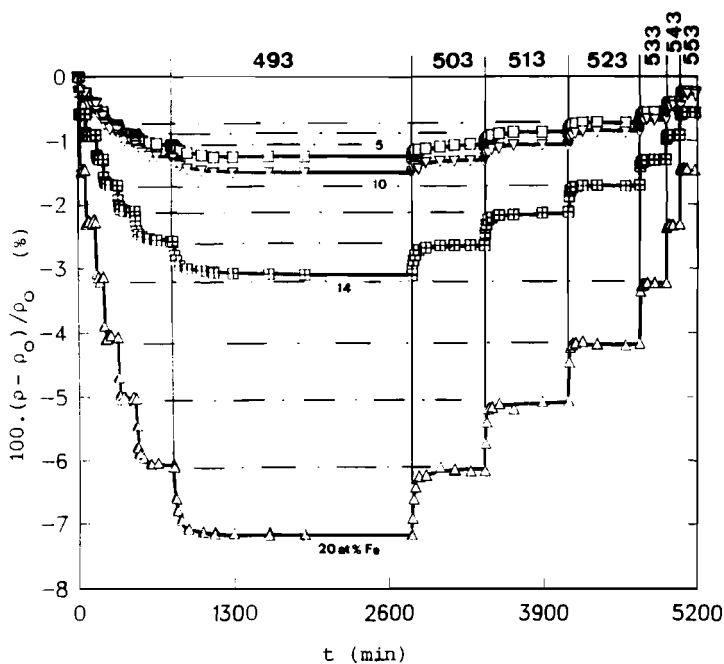


**Figure 3.** Resistivity change vs. annealing time at various neighbouring temperatures (small step annealing) of Au-5at%Fe ( $\square$ ), Au-10at%Fe ( $\nabla$ ), Au-14at%Fe ( $\square$ ) and Au-20at%Fe ( $\Delta$ ) in the recrystallized state.

able to tune the degree of SRO, this way making possible to measure spin glass properties for different states of SRO<sup>16,17</sup>.

### Mechanically Deformed Material

In Figure 2 in addition to the results on recrystallized material measurements on a sample are shown, which was cold-rolled to about 80% thickness reduction to achieve a high dislocation density (full symbols). Then the sample was annealed for 0.5 h at 573K to produce a defined state of SRO comparable to that of the recrystallized sample. It is observed that the onset of SRO-induced resistivity change is shifted to higher temperatures for the higher dislocation density in the deformed state. Obviously, quenched-in vacancies taking part in the SRO-kinetics of recrystallized samples anneal-out in the defected material at the high number of dislocations before contributing to changes in the degree of order. Fitting the above kinetic model<sup>14,15</sup> to experimental results again yielded corresponding vacancy parameters and a satisfying dislocation density (full curves in Figure2).

Investigation of SRO-kinetics in deformed  $\alpha$ -AuFe is straightforward because it could be shown that no marked changes in dislocation density occur below 650K<sup>15</sup>. This means that there is no overlap between the temperature range where SRO-kinetics is studied (below 550K) and where massive annihilation of dislocations is observed. A more difficult situation is met in  $\alpha$ -AgZn alloys, where considerable annealing of dislocations occurs in the temperature range where changes in SRO are studied<sup>18</sup>. It has been shown, however, that in this case a separation of pure changes in the degree of order from pure changes in deformation induced defect annealing can be done. This way, a study of SRO-kinetics for different states of recovery and recrystallization was made possible<sup>19</sup>. Figure 4 shows such a study for Ag-23at%Zn alloys.

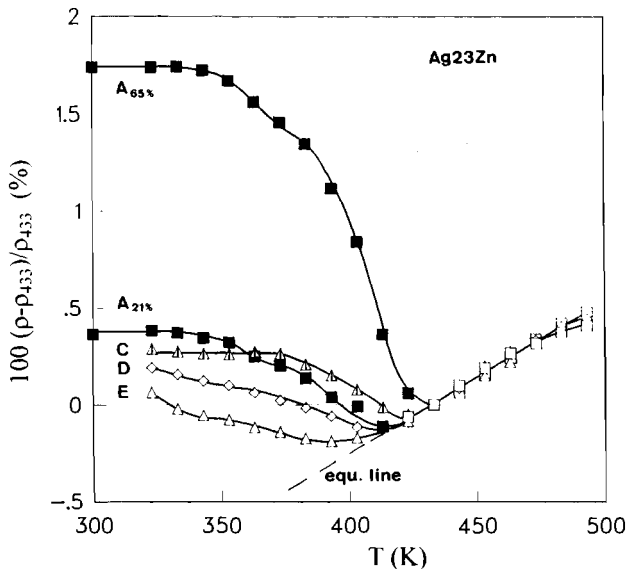


**Figure 4.** Comparison of SRO-kinetics of Ag-23at%Zn for different states of defect annealing. (■) as-rolled state A (21% and 65% thickness reduction); (▲), (◇) isochronal defect annealing to 553K (state C) and 843K (state D), respectively; (△), 3h recrystallization treatment at 843K (state E). For more details see<sup>19</sup>.

## Degree of SRO in the As-Deformed State

What occurs during deformation in a material with respect to SRO? It turned out as a main result of the above investigations that SRO develops practically undisturbed in the highly deformed alloy<sup>19</sup>. This is a consequence of inhomogeneous deformation, leaving a great part of the sample volume more or less defect free. On the other hand it is known that plastic deformation influences the instantaneous degree of SRO by the moving dislocations<sup>20</sup>. The usual picture is that the moving dislocations destroy the atomic correlations and that in this way deformation reduces the instantaneous degree of SRO<sup>21</sup>.

Such a behaviour has been observed for several alloys, including the above AgZn alloys. In this case the degree of order was the lower the higher was the degree of deformation (see Figure 4). In contrast, for Au-10at%Fe cold-rolled to about 80% thickness reduction a degree of order was observed which corresponds to that of room temperature. A plausible reason for this surprising behaviour may arise from the amount of vacancies induced during deformation process<sup>18</sup>. If this number is great enough it may restore SRO immediately behind the running dislocation. For deformation at room temperature, therefore, a degree of SRO corresponding to that of room temperature would result as a maximum value, just as actually observed.

## KINETICS OF LONG-RANGE ORDERING

### L<sub>10</sub>-Ordering in CuAu

It is known that stoichiometric CuAu undergoes two different sorts of ordering transformation, dependent on annealing temperature; tetragonal CuAuI forms below about 380-400°C and orthorhombic CuAuII between this temperature and the transition to the disordered state at about 410-420°C. A recent investigation by *in-situ* resistometry and several complementary measuring methods (residual resistometry, differential scanning calorimetry, microhardness and acoustic emission) showed that a certain temperature treatment can stabilize the CuAuI ordered phase, leading to a shift to lower temperatures of order-disorder temperature measured during continuous heating<sup>22</sup>. A detailed investigation including a study of the effect of undercooling as a function of cooling rate is under progress.

### L<sub>11</sub>-Ordering in CuPt

The alloy system Cu-Pt for Pt-concentrations between about 30at% and 80at%Pt shows a very broad stability range of the unique L<sub>11</sub> superstructure with no change in nearest neighbour configuration during ordering. A very detailed investigation of ordering kinetics by residual resistometry was done in recent years for stoichiometric and off-stoichiometric concentrations<sup>23-25</sup>. One of the aims of this investigation was a careful check of *residual resistometry* as a tool for investigating changes in the degree of LRO by parallel investigation of resistivity and X-ray diffraction after equal thermal treatment<sup>26</sup>.

Figure 5 gives the final plateau values versus temperature of a great series of isothermal annealings (small step annealing procedure) as determined by X-ray diffraction and as calculated from resistivity measurements by using the Rossiter formalism. It is shown that an excellent correspondence results for both methods. Since the experimental results in Figure 5 definitely give values of the order parameter 'in thermal equilibrium' the values may be compared with model calculations. The line in Figure 5 is calculated with a model proposed by Fournet<sup>27</sup>, which gives a satisfying correspondence up to about 800°C, but deviates slightly in the vicinity of the order/disorder temperature from both X-ray and resistivity measurement.

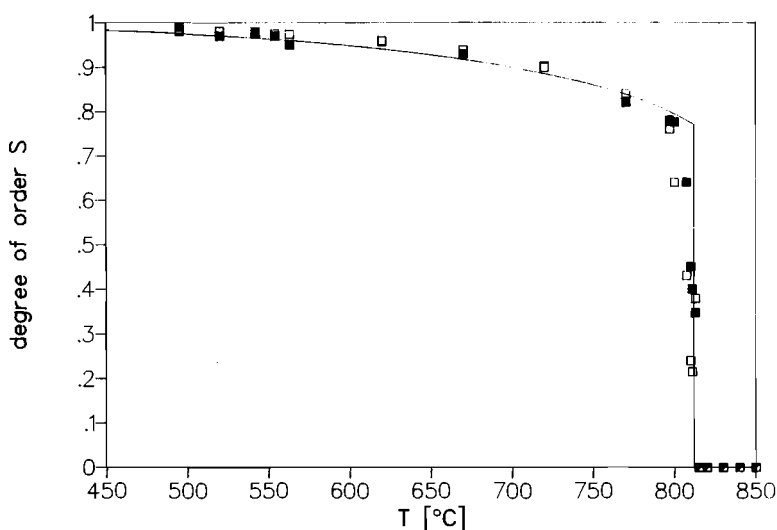


**Figure 5.** LRO-parameter  $S$  versus temperature as determined by X-ray diffraction and as calculated from resistivity measurement for  $\text{Cu}_{50}\text{Pt}_{50}$  (fit-parameter in eqn(3):  $A=0.7$ ). (■) X-rays, (□) resistivity. The curve is calculated with the Fournet model<sup>27</sup> taking for the interaction energies  $W_1=720\text{ k}$  and  $W_2=1220\text{ k}$ <sup>26</sup>.

## L1<sub>2</sub>-Ordering in $\text{Cu}_3\text{Au}$ and $\text{Ni}_3\text{Al}$

It is very well established that below  $390^\circ\text{C}$   $\text{Cu}_3\text{Au}$  undergoes a phase transformation into L1<sub>2</sub> superstructure and it is known that the sequential ordering by cooling through the transition temperature generates a network of antiphase domains. An investigation on ordering kinetics in cold-rolled and recrystallized  $\text{Cu}_3\text{Au}$  is reported in another paper of this conference<sup>28</sup>.

In contrast to  $\text{Cu}_3\text{Au}$ ,  $\text{Ni}_3\text{Al}$  remains long-range ordered right up to the melting point (direct ordering) therefore showing only very coarse domains, if any. Although highly ordered, due to thermodynamic reasons there is a tendency to a decreasing degree of LRO with increasing temperature as soon as atomic mobility allows for microstructural changes. However, such changes are extremely fine and it seems that residual resistometry is the only method at hand with high enough resolution.

A recent detailed investigation has been done on  $\text{Ni}_{76}\text{Al}_{24}+0.19\text{at\%B}$ <sup>29,30</sup>. In Figure 6 order-order relaxations between 813K and 873K are plotted versus annealing time. The reversibility of the order relaxation is clearly demonstrated as well as the very fine scale of the variation in order parameter. Within a particular relaxation the change in resistivity amounts to 0.5%, which corresponds to a change in LRO-parameter of less than 0.1%.

An analysis of the detailed order-order relaxations showed that two exponential processes of very different relaxation times are involved, yielding similarly high activation energies of 4.6eV. These two experimental results could be explained by an atomistic model of atomic jumps to next nearest vacancies<sup>31</sup>. The parallel processes are ascribed to selected jumps of atoms to vacancies on different sublattices considering different concentration of vacancies on different sublattices, the high activation energy seems to be connected with a high formation enthalpy of vacancies of the minority atoms<sup>32</sup>. Recently, the Path Probability Method as an extension of the Cluster Variation Method to kinetics was applied to L1<sub>2</sub> structure and the resistivity change during isothermal annealing at neighbouring temperatures was calculated converting the obtained LRO-parameter via eqn.(3) into resistivity change<sup>33</sup>. A good reproduction of experimental results was obtained, although only the slow relaxation process could be detected. Preliminary results of Monte-

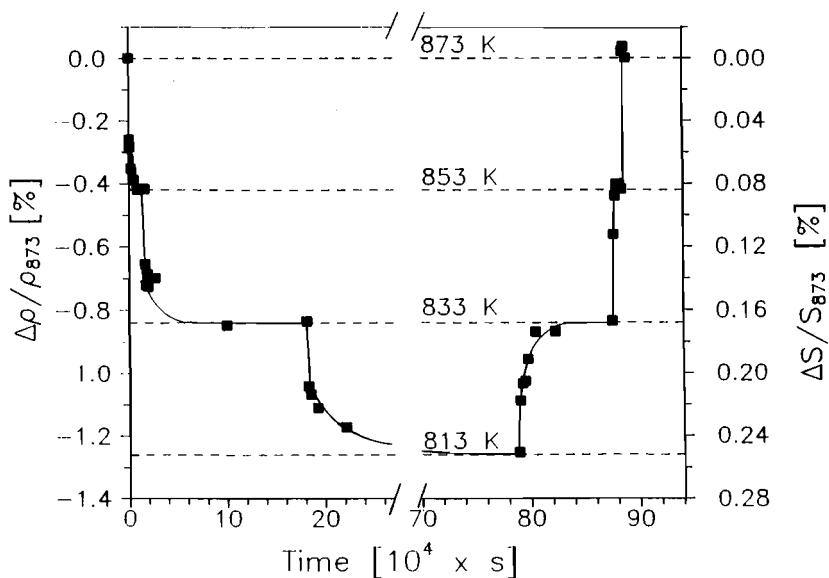


**Figure 6.** Relative change of residual resistivity and LRO-parameter of  $\text{Ni}_{76}\text{Al}_{24}+0.19\text{at}\%\text{B}$  during isothermal annealing at indicated temperatures<sup>30</sup>.

Carlo-simulations for  $\text{L1}_2$  superlattice including saddle-point energies for atomic jumps in fact yielded two-process kinetics with the ratio of the two relaxation times being correlated with the difference between the activation barriers of the two sorts of atom.

It should be emphasized here that usual tracer diffusion experiments in  $\text{L1}_2$  ordered alloys due to diffusion of majority atoms mainly over their own sublattice do not give any of the strongly desired information about ordering kinetics. The study of *order-order relaxations* in contrast, yields a *selective information* just about those atomic jump processes which are related to *ordering phenomena*.

### LRO in Mechanically Deformed Material

It is obvious that the knowledge about the evolution of LRO in deformed material is of crucial importance for the application of ordered structural materials. If ordering kinetics first has been investigated in recrystallized material it may be tried to study afterwards both ordering and recovery processes occurring simultaneously in mechanically deformed material. Such a study has been done recently on  $\text{Ni}_3\text{Al}+\text{B}$  cold-rolled to 8% and 14% thickness reduction. In Figure 7 the relative change of resistivity is plotted versus annealing temperature during isochronal annealing for two recrystallized samples, slow-cooled and quenched, respectively (full symbols). For the deformed samples isochrones of ‘pure ordering’ (open symbols) starting with plateau were constructed by subtracting from the as-measured curves (broken lines) exponential-like decrease of resistivity which is assumed to be caused by recovery of deformation induced defects starting from the lowest annealing temperatures. This assumption is in very good agreement with results of microhardness tests and investigation by electron microscopy<sup>29</sup> (drastic annealing of superlattice intrinsic stacking faults below 673K, gradual annealing of antiphase boundary dissociated superlattice dislocations).

Qualitatively, the process of re-ordering proceeds similar in deformed and homogenised samples. Yet, two differences between deformed and recrystallized samples are observed:

- (i) Differences in the initial levels of  $\Delta\rho/\rho_0$ , which reflect the different initial degree of LRO. The highest degree of LRO (lowest initial resistivity) is observed for the

slow-cooled sample S3, whereas the deformation to 14% reduction (S2) resulted in the lowest degree of LRO (highest disorder). Cold-rolling to 8% reduction corresponds to quenching a homogenised sample from 973K.

- (ii) Differences in the temperature, at which ordering (decrease in resistivity) starts. Whereas ordering in homogenised samples (S3 and S4) started at about 650K, it was shifted to lower temperatures by about 100K in the deformed case. Since we know from cooling experiments that mobility due to thermal vacancies is frozen below about 800K, ordering in Figure 7 below 800K has to be attributed to excess vacancies either quenched-in (S3 and S4) or generated by cold-rolling (S1 and S2) prior to isochronal annealing. In addition, there are hints at a slight reduction of migration enthalpy in the deformed samples<sup>31</sup>. In  $\text{Cu}_3\text{Au}$ , which can be deformed in the ordered and disordered state, we observed a similar shift to lower temperatures of atomic mobility for the case of deformation in the ordered case, whereas ordering started practically without excess vacancies in the case when deformed in the disordered state. Since deformation in  $\text{Ni}_3\text{Al}$  always is done in a highly ordered

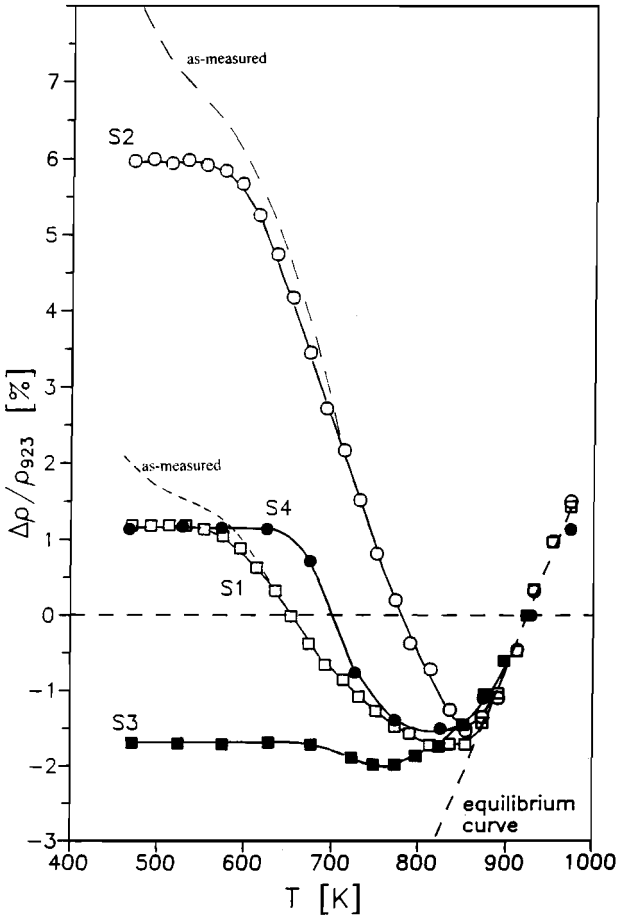


**Figure 7.** Resistivity change during isochronal annealing of  $\text{Ni}_{76}\text{Al}_{24+0.19\text{at}\%}\text{B}$  ('pure ordering') after separating 'non-ordering' effects of defect recovery from as-measured curves (broken line). For more details see<sup>29</sup>. S1(□) 8% reduction, S2(O) 14% reduction, S3(■) slow-cooling, S4(●) quenched from 973K.



state, results in both materials hint at a high production of vacancies by cold-rolling in the ordered state.

Applying the model of vacancy-controlled ordering to isochronal curves of deformed samples yielded vacancy parameters in correspondence with results on recrystallized materials and experimental results of small step annealing.

### Competition Between LRO and SRO

Whereas only a few atomic jumps may be necessary to enable changes in the equilibrium degree of SRO, without atomic movement over long distances changes in LRO may not be sufficient to reach equilibrium. This can lead to a competition between increase of SRO in the matrix and formation of the new LRO-phase when lowering the temperature below an order/disorder phase boundary. In those cases, thermal and/or mechanical pre-treatment of the sample is of crucial importance for what is observed in the sample.

Such a behaviour of metastability has been reported in the systems  $\text{Cu}_{65}\text{Pt}_{35}$ <sup>24</sup> and  $\text{CuAu}_3$ <sup>34</sup>. It has been shown that for increased annealing time or after mechanical deformation LRO is obtained, whereas for too short annealing times in homogenised material only the variation of SRO with temperature is detected. This may lead to serious misinterpretation of alloy stability if not carefully enough investigated.

### CONCLUSIONS AND FUTURE ASPECTS

It has been shown that *residual resistometry* gives detailed information about SRO-and LRO-kinetics, in particular:

**SRO:**

- SRO-relaxation kinetics yielding SRO-relaxation times and activation enthalpies;
- vacancy properties ( $H_m$  and  $H_i$ ), direct or by comparison with model calculations;
- evolution of SRO in a deformed structure, annihilation behaviour of defects;
- degree of SRO in the as-deformed state.

**LRO:**

- a) starting from the completely disordered state: formation of antiphase domains,
- b) order-order relaxations, changing the number of antisites on particular sublattice: selective observation of atomic jump mechanism;
- ordering activation energy
- interaction of LRO and deformation.

There is still need for more detailed investigation of atomic jump processes and of interaction of ordering and deformation. Aside of this, three future aspects seem to be of main importance:

- (i) What is the reason for deformation sometimes *increasing* the degree of SRO?
- (ii) Study of order-order relaxations in B2-ordered alloys.
- (iii) More rigorous approach in calculating SRO- and LRO-induced resistivity changes.

### Acknowledgements

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## **ELECTRONIC STRUCTURE AND TRANSPORT**

# IMPROVED LMTO-ASA METHODS PART II: TOTAL ENERGY

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## INTRODUCTION

In this paper we will present a way to improve the evaluation of total energies in LMTO calculations. The Kohn Sham energy functional [1] can be written in the form

$$E[\rho] = T[\rho] + E_{xc}[\rho] + \underbrace{\int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' + \int \rho(\mathbf{r})V_{nuc}(\mathbf{r}) d^3\mathbf{r} + \sum_{\mathbf{R}, \mathbf{R}'} \frac{Z_{\mathbf{R}}Z_{\mathbf{R}'}}{|\mathbf{R} - \mathbf{R}'|}}_{\text{Electrostatic energy (} E_{ES} \text{)}}$$

Consider the electrostatic terms. These are hard to evaluate because the output charge density is a complicated non spherical function in space. In traditional LMTO calculations the charge density is first *spheridised* before  $E_{ES}$  is calculated. In this method  $\rho(\mathbf{r})$  is reduced to a sum of spherically symmetric balls of charge inside each ASA sphere [2].

$$\rho(\mathbf{r}) \Rightarrow \sum_{\mathbf{R}} \rho_{\mathbf{R}}(|\mathbf{r} - \mathbf{R}|)$$

The electrostatic energy is then calculated for this system of charge [2], giving

$$E_{ES}^{ASA} = \sum_{\mathbf{R}} \int_{|\mathbf{r}-\mathbf{R}| < s_{\mathbf{R}}} \rho_{\mathbf{R}}(|\mathbf{r}-\mathbf{R}|) \left[ -2 \frac{Z_{\mathbf{R}}}{|\mathbf{r} - \mathbf{R}|} + \int_{|\mathbf{r}'-\mathbf{R}| < s_{\mathbf{R}}} \frac{\rho_{\mathbf{R}}(|\mathbf{r}' - \mathbf{R}|)}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' \right] d^3\mathbf{r} + V_{mad}$$

The consequences of this approximation are well known. While  $E_{ES}^{ASA}$  is good enough for calculating bulk moduli it will fail for deformations of the crystal that do not preserve symmetry. So it cannot be used to calculate, for example, shear elastic constants or phonons. The reason is simple.  $E_{ES}^{ASA}$  changes little if you rotate one atomic sphere about another. Therefore while  $E_{ES}^{ASA}$  has the correct dependence on bond lengths, it does not have the correct dependence on bond angles. More importantly this expression fails in the absence of a set of space filling ASA spheres. There are calculations one may wish to do where this can arise, and such cases can be treated by the new LMTO

method under development. We refer the reader to the paper by O.K Andersen in the same volume [3], to which this paper is intended as a continuation.

We therefore require a new way to evaluate  $E_{ES}$ , and we will need to retain the full, non spherical, charge density  $\rho(\mathbf{r})$ .

### THE BASIC IDEA: EXPANSION IN SSW's

The SSW's (screened spherical waves) and their accompanying hard core spheres were defined in [3,4] and we assume the reader is familiar with their definition.

At each atomic site we place a set of hard core spheres with radii  $a_{\mathbf{RL}}$ . We do not place hard cores at the position of any empty spheres. These are simply ignored. The hard core spheres divide space into atomic (inside the  $a$  spheres) and interstitial (outside the  $a$  spheres) parts. In the atomic region a spherical harmonic expansion of the charge density can easily be made.

$$\rho^a(\mathbf{r}) = \sum_{\mathbf{RL}} \rho_{\mathbf{RL}}(r_{\mathbf{R}}) Y_L$$

We will refer to this as the one center expansion. The components  $\rho_{\mathbf{RL}}$  are easily calculated in LMTO and are known on a radial mesh. In the interstitial region we choose to expand the charge density in the SSW's  $|\psi\rangle$  and their first two energy derivatives.

$$\rho^i(\mathbf{r}) = \sum_{\mathbf{RL}} A_{\mathbf{RL}} |\psi_{\mathbf{RL}}\rangle + B_{\mathbf{RL}} |\dot{\psi}_{\mathbf{RL}}\rangle + C_{\mathbf{RL}} |\ddot{\psi}_{\mathbf{RL}}\rangle \tag{1}$$

The SSW form an ideal expansion set as their shape is determined by the crystal structure. Hence only a few are required. This expansion can be formulated in both real and reciprocal space, which should make the method applicable to non periodic systems. When formulated in real space all the matrix multiplications and inversions become  $O(N)$ . This makes the method comparably fast for cells large than the localisation length of the SSW. In addition once the expansion is made, Poisson's equation can be solved exactly, and the integrals over the intersitital region can be calculated exactly.

### CALCULATING THE COEFFICIENTS $A_{\mathbf{RL}}$ , $B_{\mathbf{RL}}$ , $C_{\mathbf{RL}}$

The first step is to use  $|\psi\rangle$  and  $|\dot{\psi}\rangle$  to create a fitted charge density that has the same value and slope as the true charge density on the hard core spheres. This is thus a continuous, differentiable fit. As input we need the value and slope of the charge density on the  $a$  spheres. This is directly obtainable form the one center expansion.

$$\rho_{\mathbf{RL}}(a_{\mathbf{RL}}), \qquad \left. \frac{d\rho_{\mathbf{RL}}(r)}{dr} \right|_{r=a_{\mathbf{RL}}}$$

The SSW's are solutions to the wave equation in the interstitial with energy  $\kappa^2$  and which satisfy the following boundary conditions [3,4].

|                                    | value at $\mathbf{R}'$               | radial slope at $\mathbf{R}'$                                 |
|------------------------------------|--------------------------------------|---------------------------------------------------------------|
| $ \psi_{\mathbf{RL}}\rangle$       | $\delta_{\mathbf{R}'\mathbf{R}} Y_L$ | $-a_{\mathbf{R}'L'} S_{\mathbf{R}'L',\mathbf{RL}} Y_L'$       |
| $ \dot{\psi}_{\mathbf{RL}}\rangle$ | 0                                    | $-a_{\mathbf{R}'L'} \dot{S}_{\mathbf{R}'L',\mathbf{RL}} Y_L'$ |

The  $S$  are the structure constants. From these we form the linear combinations

$$|\Theta\rangle = |\psi\rangle - |\dot{\psi}\rangle \dot{S}^{-1} S \quad (2)$$

$$|\Sigma\rangle = |\dot{\psi}\rangle \dot{S}^{-1} \quad (3)$$

which have value and slope on the hard core spheres given by

$$\begin{array}{ccc} & \text{value at } \mathbf{R}' & \text{radial slope at } \mathbf{R}' \\ |\Theta_{\mathbf{RL}}\rangle & \delta_{\mathbf{R}'\mathbf{R}} Y_L & 0 \\ |\Sigma_{\mathbf{RL}}\rangle & 0 & -a_{\mathbf{R}',L} \delta_{\mathbf{R}'\mathbf{R}} Y_L \end{array}$$

The continuous differentiable fit is then trivial and is given by

$$\rho_{cd}^i = \sum_{\mathbf{R},L} |\Theta_{\mathbf{RL}}\rangle \rho_{\mathbf{RL}}(a_{\mathbf{RL}}) - |\Sigma_{\mathbf{RL}}\rangle \frac{1}{a_{\mathbf{RL}}} \left. \frac{d\rho_{\mathbf{RL}}(r)}{dr} \right|_{r=a_{\mathbf{RL}}} \quad (4)$$

Inserting (2,3) into (4) gives the coefficients for a continuous and differentiable expansion.

$$\rho_{cd}^i = \sum_{\mathbf{R},L} |\psi_{\mathbf{RL}}\rangle \rho_{\mathbf{RL}} - |\dot{\psi}_{\mathbf{RL}}\rangle \left[ \sum_{\mathbf{R}',L'} \dot{S}_{\mathbf{RL},\mathbf{R}'L'}^{-1} \rho_{\mathbf{R}'L'} - \dot{S}^{-1} S_{\mathbf{RL},\mathbf{R}'L'} \frac{1}{a_{\mathbf{R}'L'}} \frac{d\rho_{\mathbf{R}'L'}}{dr} \right] \quad (5)$$

In practice such a fit is good, but not good enough. The error  $\rho(\mathbf{r}) - \rho_{cd}^i(\mathbf{r})$  is zero on the  $a$  spheres and maximum in the center of the interstitial. We therefore expand our basis set and introduce the second energy derivative  $|\ddot{\psi}\rangle$ . This is done by forming the function

$$|\Delta\rangle = |\dot{\psi}\rangle - |\ddot{\psi}\rangle \ddot{S}^{-1} \dot{S},$$

which has neither value nor slope on the  $a$  spheres. We perform a least squares fit to the error  $\rho(\mathbf{r}) - \rho_{cd}^i(\mathbf{r})$  using the  $|\Delta\rangle$ . This is done by sampling all three functions at a set of randomly chosen points in the interstitial.

Typically we fit up to the  $l = 3$  components of the one center expansion. This gives a maximum of 16 components (some may be zero from the crystal symmetry). For the lowest symmetry structures we thus have 48 basis functions per atom. For silicon this number reduces to 6 per atom. The number of random points required depends upon the volume of the interstitial region. On average we require a few tens of points for each missing empty sphere. In order to get well localised SSW's we use a negative energy.

## SOLUTION OF POISSON'S EQUATION

We wish to find the electrostatic potential produced by a charge density of the form given in equation (1). To do this we use the following properties of the SSW.

$$\begin{aligned} \nabla^2 |\psi\rangle &= -\kappa^2 |\psi\rangle \\ \nabla^2 |\dot{\psi}\rangle &= -\kappa^2 |\dot{\psi}\rangle - |\psi\rangle \\ \nabla^2 |\ddot{\psi}\rangle &= -\kappa^2 |\ddot{\psi}\rangle - 2|\dot{\psi}\rangle \end{aligned}$$

We also introduce the zero energy SSW,  $|\psi^0\rangle = |\psi(\kappa^2 = 0)\rangle$ . The solution to Poisson's equation  $\nabla^2 V = -8\pi\rho$  is then

$$V(\mathbf{r}) = V^0 + \sum_{\mathbf{RL}} v_{\mathbf{RL}}(r_{\mathbf{R}}) Y_L + \frac{8\pi A_{\mathbf{RL}}}{\kappa^2} (|\psi_{\mathbf{RL}}\rangle - |\psi_{\mathbf{RL}}^0\rangle) + \frac{8\pi B_{\mathbf{RL}}}{\kappa^2} \left( |\dot{\psi}_{\mathbf{RL}}\rangle - \frac{1}{\kappa^2} (|\psi_{\mathbf{RL}}\rangle - |\psi_{\mathbf{RL}}^0\rangle) \right) + \frac{8\pi C_{\mathbf{RL}}}{\kappa^2} \left( |\ddot{\psi}_{\mathbf{RL}}\rangle - \frac{2}{\kappa^2} \left( |\dot{\psi}_{\mathbf{RL}}\rangle - \frac{1}{\kappa^2} (|\psi_{\mathbf{RL}}\rangle - |\psi_{\mathbf{RL}}^0\rangle) \right) \right), \quad (6)$$

as can be seen by applying  $\nabla^2$ . The term  $V^0$  is the Laplace part of the solution ( $\nabla^2 V^0 = 0$ ). It is chosen to make the potential everywhere continuous, differentiable and non divergent. It can be expanded exactly and easily in terms of the SSW  $|\psi^0\rangle$ . The  $v_{\mathbf{RL}}$  are obtained from  $\rho_{\mathbf{RL}}$  by standard numerical techniques which we shall therefore not discuss. At this point the potential of the spherically symmetric cores and the nuclei can be added. They can be absorbed into  $v_{\mathbf{RL}}$  and  $V^0$ .

To obtain the  $E_{ES}$  we must now integrate the product of  $\rho$  and  $V$ . In the atomic region we have a numerical integrals on a radial mesh. In the interstitial we have integrals of products of SSW's. These can always be reduced to expressions involving the structure constants and their energy derivatives, all of which are known [3,4].

## RESULTS FOR SILICON, AND SUMMARY

In figure 1 we show both the true charge density and our expansion along the [111] direction. This shows that the expansion is indeed a good representation of the charge density.

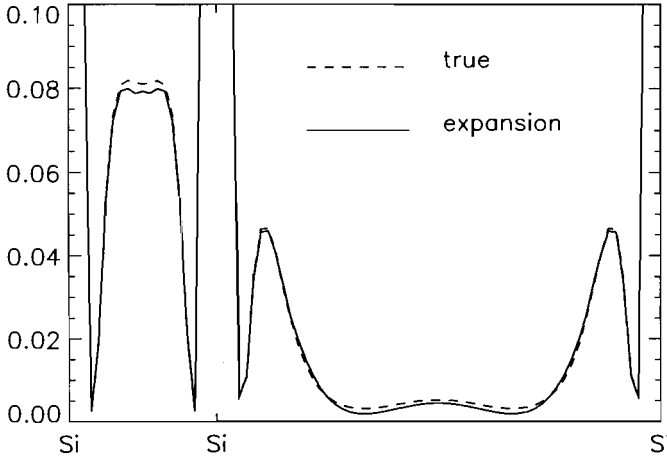


**Figure 1.** True charge density and the expansion (as described in the text), for silicon. The [111] direction is shown. The parameters used were  $a_{\mathbf{RL}} = 2.5$  au and  $\kappa^2 = -1.5$  Ryd.

In figure 2 we show the difference between electrostatic energy calculated by the new method,  $E_{ES}^{new}$ , and  $E_{ES}^{ASA}$ . This shows that the variation of  $E_{ES}^{new}$  with the choice of

the expansion parameters  $a, \kappa^2$  is less than 0.1eV. The variation with  $\kappa^2$  reduces with decreasing interstitial volume. For  $a > 0.22$  au the hard core spheres will overlap. Due to the boundary conditions imposed on them, the SSW's will become hard to localise as this overlap increases. This effect is responsible for the fluctuation of  $E_{ES}^{new}$  for large values of  $a$ . We can also see that for  $\kappa^2$  close to -1.25 Ryd there is practically no variation in  $E_{ES}^{new}$  with the hard core radii  $a$ . In the interstitial region the potential is fairly smooth. This means that the wave-functions should fall off approximately like  $\exp(-\sqrt{\epsilon}r)$ , where the energy  $\epsilon$  is close to the difference between the band center and the top of the interstitial potential. For silicon this gives 0.3 Ryd. The charge density should then fall of in the interstitial like  $\exp(-\sqrt{4\epsilon}r)$ . Thus in silicon the interstitial charge density has a characteristic energy that is close to  $-0.3 \times 4 = -1.2$  Ryd.

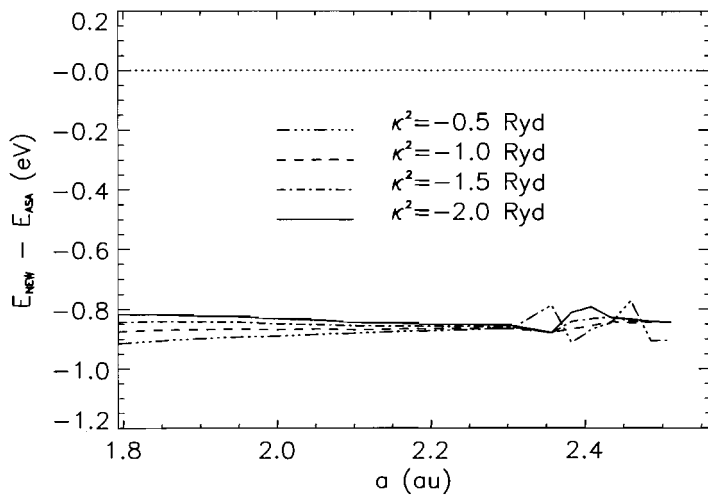


**Figure 2.** The difference between  $E_{ES}^{new}$  and  $E_{ES}^{ASA}$  per atom for silicon.

To summarise, we have presented a way to improve an LMTO-ASA calculation of the electrostatic energy in a crystal. The method is stable and general in its formalism so that it should be applicable to a wide range of systems. In this talk we did not mention the exchange correlation energy. It is possible to make an expansion of the  $\epsilon_{xc}(\rho(\mathbf{r}))$  in terms of the SSW's. Then the integral

$$E_{XC} = \int \epsilon_{xc}(\rho(\mathbf{r}))\rho(\mathbf{r}) d^3\mathbf{r}$$

is easily evaluated. In this way we can improve on the evaluation of the whole energy functional. This, and the application to elastic constants, is work in progress.

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## EFFECTS OF INTERFACE INTERMIXING ON THE MAGNETIC INTERLAYER COUPLING

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After the discovery of the oscillatory magnetic interlayer coupling between ferromagnetic films separated by a paramagnetic spacer<sup>1,2</sup> these sandwiched systems have been a subject of intense research. There have been many attempts to explain the magnetic interlayer coupling and a great number of theoretical and experimental studies have been performed<sup>3,4</sup>.

One conceptually very important way to gain understanding of physical phenomena has been to compare experiments with theory. In modern physics we usually compare experimental data with the results calculated from the basic postulates of quantum mechanics. However, a fundamental difficulty arises when the experimental conditions are not fully known or do not represent equilibrium. In the case of magnetic multilayers one major problem of comparing theoretical calculations with experimental data is to understand to what extent the found discrepancy is due to the roughness of the interface between the para- and ferromagnetic layers existing in the experimental samples. Since these kinds of layered systems are not in equilibrium most defects have to be introduced ad hoc in theoretical calculations. In earlier attempts one has usually tried to model the roughness by an averaging of the coupling strength over different spacer thicknesses<sup>5</sup>. This approach is close to the limit when the roughness consists of large flat plateaus of different heights. In this case the system corresponds to an ensemble of perfectly sandwiched layers with different spacer thicknesses. However, when the plateaus are of atomic size the averaging procedure is hard to justify and might give misleading results. In this work we have tried to model the interface roughness, in the limit of the atomic length scale of the roughness, by a random intermixing, i.e. a binary alloy, within a single monolayer at each of the two interfaces between the paramagnetic spacer and the surrounding ferromagnetic crystals. Calculations with a similar approach has recently been performed by Kudrnovský *et al.* for a Co/Cu/Co (001) system<sup>6</sup>. A more realistic

description of the interfaces may of course take into account a combination of different types of defects such as intermixing ranging over several layers around each interface as well as plateaus, dislocations and interface relaxations.

As examples for our investigation we have chosen Fe/Cu/Fe bcc (001) and Co/Cu/Co fcc (001) trilayers. A trilayer consists of two semi infinite crystals of Fe separated by a paramagnetic Cu spacer. The entire trilayer has the same crystal structure which means that all effects from lattice relaxations are excluded. The experimental lattice constant of bcc Fe was chosen for the Fe/Cu/Fe bcc trilayers, whereas for the Co/Cu/Co fcc trilayers we used the lattice constant of fcc Cu.

The present calculations were performed by means of the interface Green's function technique, developed by Skriver and Rosengaard<sup>7</sup>. It is based on the linear muffin-tin orbitals (LMTO) method<sup>8,9</sup> within the tight-binding representation<sup>10,11</sup>, frozen core, and atomic-sphere approximations (ASA) together with the local spin density approximation in the parametrization by Vosko, Wilk and Nusair<sup>12</sup>. The application of a Green's function technique ensures a correct description of the loss of translational symmetry perpendicular to the interfaces. Furthermore, the application of the principle layer technique<sup>13</sup> leads to a high computational efficiency which scales essentially linearly with the number of atomic monolayers. To include the effects of intermixing the coherent potential approximation (CPA) has been used in combination with the interface Green's function technique<sup>14</sup>. For each intermixed atomic monolayer, which is treated as a binary alloy, the coherent-potential is calculated for the construction of the principal layers. The Green's function for the principal layers are recalculated and joined together by means of the principal layer technique and charge densities, potential and potential parameters are calculated self-consistently. The procedure is repeated until the total energy converges within 1  $\mu$ Ry, well beyond the values of the coupling energies.

In order to calculate the magnetic interlayer coupling,  $J(N)$ , we calculated the difference between the total energy of the self-consistent antiferromagnetic (AF) configuration, where the magnetization in the two semiinfinite ferromagnetic crystals is aligned antiparallel, and the corresponding ferromagnetic (FM, parallel) configuration, i.e.

$$J(N) = E_{tot}^{AF} - E_{tot}^{FM}, \quad (1)$$

as a function of the number of atomic monolayers (ML),  $N$ , in the paramagnetic spacer.

In Fig. 1 we display the magnetic interlayer coupling for pure Fe/Cu/Fe bcc (001) trilayers, without interface intermixing, together with the coupling for the corresponding dilute trilayers with a random binary Fe<sub>0.50</sub>Cu<sub>0.50</sub> alloy in a single monolayer at each Fe/Cu interface. The intermixing decreases the amplitude of the interlayer coupling by almost one order of magnitude and the AF coupling disappears totally. It is interesting to note that it would be difficult to understand the disappearance of the AF coupling in the dilute case by a simple averaging over different spacer thicknesses of the interlayer coupling for perfect interfaces. As a comparison we show one example of an averaged interlayer coupling in Fig. 1. In the experiments the 2 ML oscillations between FM and AF coupling were not seen for spacers between 6 and 12 ML<sup>15</sup>, whereas in the long range limit (10 to 18 ML) a 2 ML oscillation was indeed found<sup>16</sup>. The length scale of the interface roughness may therefore be important even for the qualitative behaviour of the magnetic interlayer coupling.

In Fig. 2 we show the coupling energy as a function of interface mixing with 5 ML of pure Cu in the spacer. The coupling strength decreases almost linearly with increased intermixing and changes sign somewhere between 40 and 50% of intermixing. A

change of the interface mixing will thus continuously increase or decrease the interlayer coupling.

In Fig. 3 we show the magnetic interlayer coupling for pure Co/Cu/Co fcc (001) trilayers together with the corresponding dilute trilayers with the maximal Co/Cu intermixing (50% of each atomic type) in a single monolayer at the interfaces. The interlayer coupling is decreased by approximately a factor of 2 due to the introduction of the interface roughness. The decreasing of the coupling strenght is in qualitative agreement with the results by Kudrnovský *et al.*, however obtained with a slightly different type of interface intermixing<sup>6</sup>. In the long range limit ( $>8$  ML) the periodicity of the two curves in Fig. 3 coincide. This is in full agreement with RKKY-like theory<sup>4</sup>, which states that the periodicity of the interlayer coupling should, at least in the limit of infinite spacer thickness, be governed by the extremal spanning vectors of the paramagnetic bulk Fermi surface. This connection has also been confirmed by first principles calculations<sup>17,5</sup>. The periodicity of the coupling for thick spacers will therefore essentially not be influenced by the interface roughness. The introduction of roughness may thus in the long range limit only change the amplitude and phase of of the interlayer coupling, not the periodicity.

In Fig. 4 we show how the interlayer coupling strength is decreasing continuously as a function of the intermixing concentration. The behaviour is very similar to the case of interface intermixing in Fe/Cu/Fe trilayers shown in Fig. 2.

By means of self-consistent total energy calculations the sensitivity on interface roughness of the magnetic interlayer coupling in Fe/Cu/Fe bcc (001) and Co/Cu/Co fcc (001) trilayers has been investigated. The coupling energy was shown to decrease as an effect of the interface mixing. A change of the interface mixing may substantially change the coupling energy, whereas the periodicity of the coupling in the long range limit as a function of spacer thickness is not affected, in full accordance with RKKY-like theory. The coupling energy for Fe/Cu/Fe bcc (001) trilayers with maximal interface intermixing (50%) could not be reproduced by a simple averaging of the interlayer coupling for trilayers with perfect interfaces. The interlayer coupling appears thus to

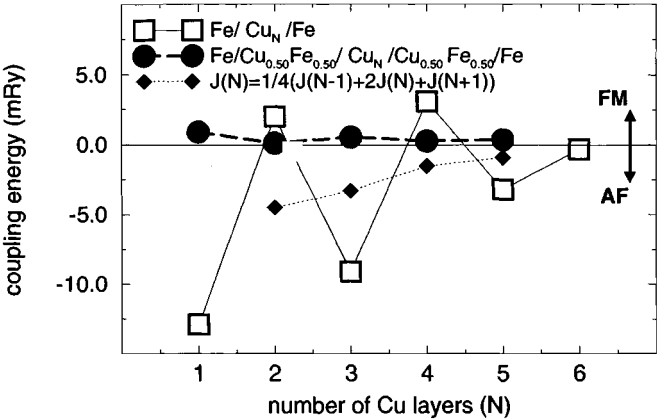


**Figure 1.** The magnetic interlayer coupling in Fe/Cu/Fe bcc (001) trilayers. The squares denote the coupling energies for the pure trilayer and the circles the coupling energies for the dilute trilayers with 50% of intermixing in a single monolayer at each Fe/Cu interface. One example of an averaged interlayer coupling is indicated by the diamonds.

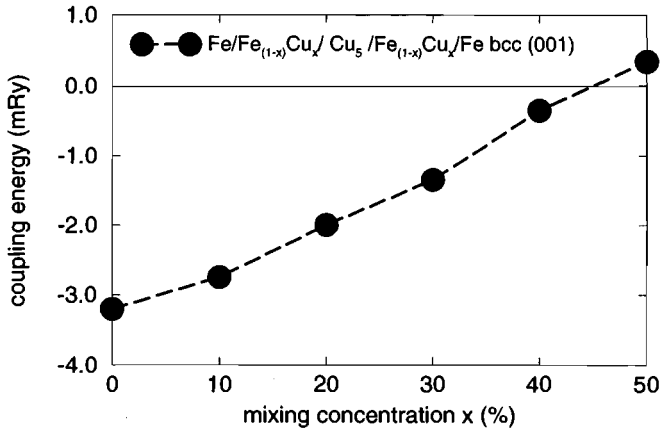


**Figure 2.** The coupling energy as a function of the intermixing concentration of the interfaces.

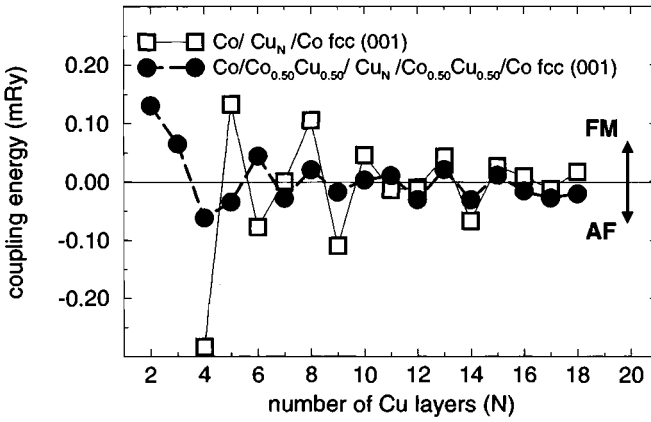


**Figure 3.** The magnetic interlayer coupling in Co/Cu/Co fcc (001) trilayers. The squares denotes the coupling energies for the pure trilayer and the circles the coupling energies for the dilute trilayers with 50% of intermixing in a single monolayer at each Co/Cu interface.

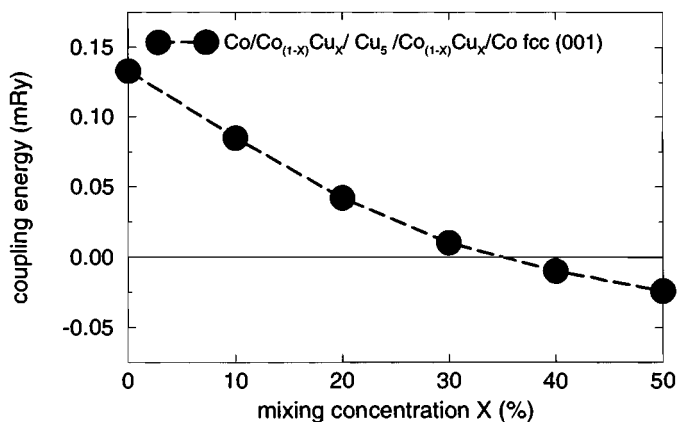


**Figure 4.** The coupling energy as a function of the intermixing concentration of the interfaces.

be sensitive to the size of the roughness at least for this specific case of Fe/Cu<sub>N</sub>/Fe trilayers with N<6. The averaging procedure may therefore give misleading results in case of interface roughness on an atomic length scale.

A more detailed analysis of these systems will be published elsewhere.

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# RELATIVISTIC CALCULATIONS OF PHOTOEMISSION- AND LEED-INTENSITIES FOR ORDERED AND DISORDERED ALLOYS: APPLICATION TO $\text{Cu}_3\text{Pt}$ and $\text{Cu}_5\text{Pt}_3$

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## INTRODUCTION

The description of the electronic structure of binary alloy surfaces is of both fundamental and technological interest. In particular alloys containing platinum offer attractive properties in the field of heterogeneous catalysis. Catalytic reactions, on the other hand, strongly depend on the electronic and geometric structure of a solid surface. For the investigation of the electronic properties of clean and adsorbate-covered surfaces and thin films, angle-resolved photoemission spectroscopy has developed into an important tool, because this experimental technique allows measuring the band dispersions to a high degree of accuracy. In order to interpret the experimental data it is useful to have a quantitative comparison between calculated and measured data. Therefore we present in this contribution theoretical and experimental photoemission- and LEED-intensities of a surface alloy consisting of a few layers of  $\text{Cu}_3\text{Pt}$  on a  $\text{Pt}(100)$  substrate. Furthermore, we show results for a species found to be  $\text{Cu}_5\text{Pt}_3$  on Pt. Finally, we compare the photoemission intensities from an ordered  $\text{Cu}_3\text{Pt}$  and a disordered  $\text{Cu}_{75}\text{Pt}_{25}$  bulk phase. To our knowledge, this is the first time that photoemission intensities were calculated for an alloy overlayer on a metal surface.

The calculations were performed in the framework of a one-step model of photoemission derived from the one originally formulated by Pendry [1]. Nowadays the model includes relativistic effects [2-5], the possibility of having several atoms per unit cell [6], different types of layers and a realistic model for the surface potential [7]. It is further possible to consider overlayers on a surface. We will not review the theory here, which has been done already in several publications [2,4,6,8], but instead concentrate on the results.

The experimental investigation was performed by depositing copper films on the (100)-surface of a platinum single crystal. It was found that the reconstruction of the Pt surface was lifted upon Cu adsorption. The system was then heated to different temperatures and the formation of different ordered surface alloys was evidenced by

LEED, namely one with a  $c(2 \times 2)$  and one with a  $p(2 \times 2)$  superstructure. They are compatible with  $\text{Cu}_3\text{Pt}$  and  $\text{Cu}_5\text{Pt}_3$  layers. The first atomic layer was in both cases found by means of photoemission of adsorbed xenon to be pure copper. Details of the experimental work can be found in ref. 9 and 10. A schematic view of both structures can be seen in figure 1. Both consist of alternating layers of pure copper and of mixed composition. In the  $\text{Cu}_3\text{Pt}$  case, the second and all other evenly numbered layers have equal numbers of copper and platinum atoms, whereas in the  $\text{Cu}_5\text{Pt}_3$  case the evenly numbered layers consist of thrice as many platinum as copper atoms.

The paper is organized as follows: we begin with the results for the  $\text{Cu}_3\text{Pt}$  single crystal, the layer sequence of which is depicted in the left panel of figure 2. We then proceed to the  $\text{Cu}_3\text{Pt}$  overlayer on the  $\text{Pt}(100)$  substrate. The structure can be seen in the middle panel of figure 2. We then step to a more complicated system, namely to the  $\text{Cu}_5\text{Pt}_3$  overlayer on the same substrate (see right panel of figure 2). Last but not least the comparison of the ordered phase of  $\text{Cu}_3\text{Pt}$  with the disordered  $\text{Cu}_{75}\text{Pt}_{25}$  will conclude the presentation of the results, which will then be summed up.

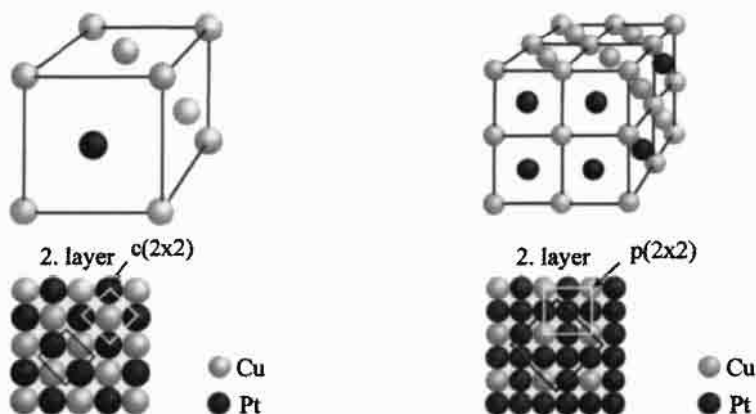


Figure 1: Schematic views of the  $\text{Cu}_3\text{Pt}$  (left panel) and  $\text{Cu}_5\text{Pt}_3$  (right panel) ordered structures. The squares indicate the unit cells.

## RESULTS FOR THE $\text{Cu}_3\text{Pt}$ CRYSTAL

The TB-LMTO bandstructure of  $\text{Cu}_3\text{Pt}$ , which we used for our photoemission calculations, is due to A. Postnikov [11]. We first calculated the photoemission intensities for HeI radiation for different angles of incidence on the (100) surface of an ordered  $\text{Cu}_3\text{Pt}$  crystal in the azimuthal direction  $20^\circ$  off the  $\langle 100 \rangle$  direction, the same that was used in the experiment, and compared these with the experimental results for an alloy overlayer on the platinum substrate. The theoretical results are shown in the left panel and the experimental findings in the middle panel of figure 3. The angle between the directions of photon incidence and electron emission was always  $60^\circ$ . The agreement of the main features is good, the dispersion of the peak is clearly reproduced, but there are extra intensities in the experimental spectra near the Fermi energy and at about -5 eV which originate from the substrate, as will be shown in the next section.



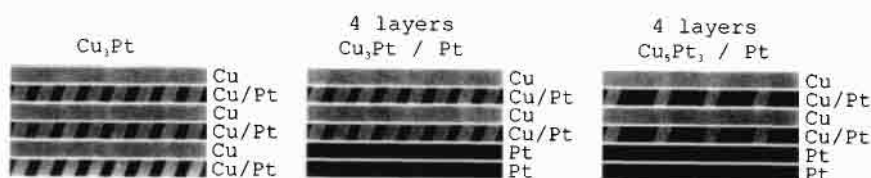


Figure 2: Schematic views of the layer sequence of the ordered structures discussed in the text: the  $\text{Cu}_3\text{Pt}$  single crystal (left panel), the ordered overlayer of  $\text{Cu}_3\text{Pt}$  on the Pt substrate (middle panel) and the ordered overlayer of  $\text{Cu}_5\text{Pt}_3$  on Pt (right panel).

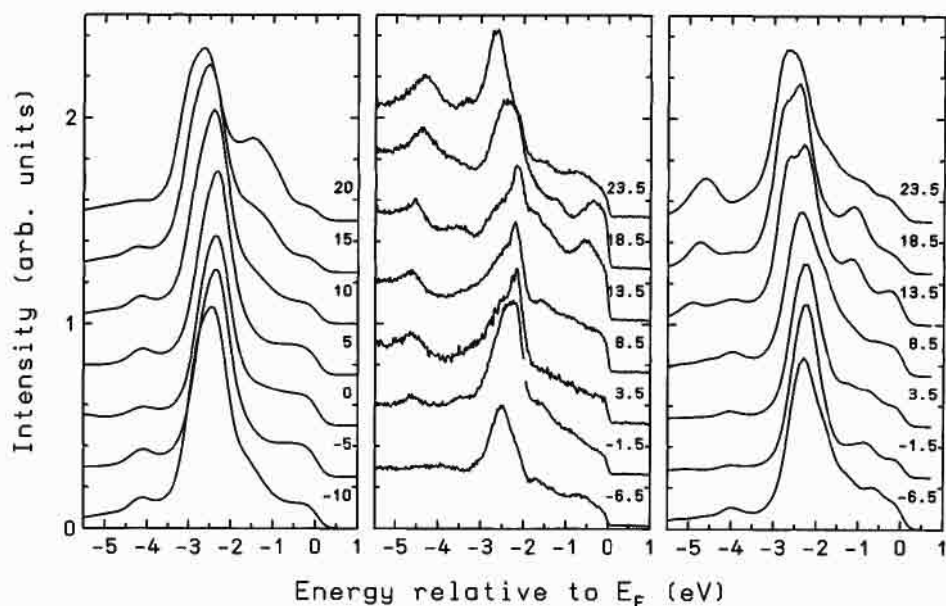


Figure 3: Left panel: calculated HeI excited photoemission intensities for a  $\text{Cu}_3\text{Pt}(100)$  single crystal surface;

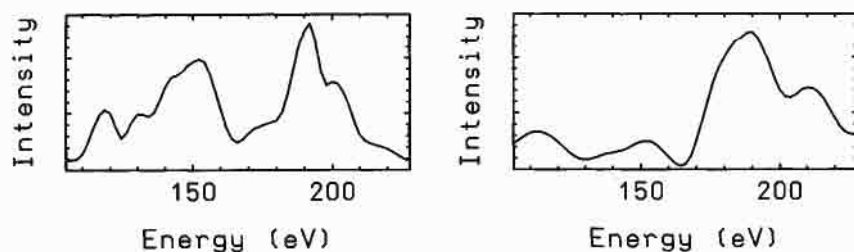


Figure 4: Calculated (left panel) and measured (right panel) LEED-intensities for the (10)-beam from an ordered  $\text{Cu}_3\text{Pt}$  layer on a Pt(100) substrate.

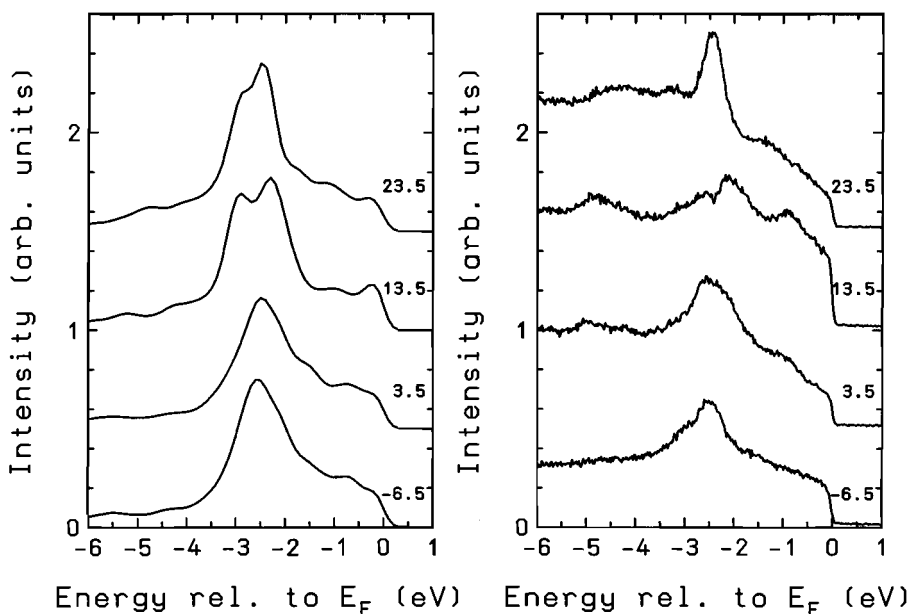


Figure 5: Calculated (left panel) and measured (right panel) HeI excited photoemission intensities for a  $\text{Cu}_5\text{Pt}_3$  layer on a Pt(100) surface. The curves are labeled with their emission angles.

middle panel: experimental findings for a  $\text{Cu}_3\text{Pt}$  overlayer on a Pt(100) substrate;  
 right panel: calculated photoemission intensities for a four layer  $\text{Cu}_3\text{Pt}$  overlayer on a Pt substrate. The curves are labeled with their emission angles.

## RESULTS FOR A $\text{Cu}_3\text{Pt}$ OVERLAYER ON A Pt SUBSTRATE

The next step was then to simulate a four layer  $\text{Cu}_3\text{Pt}$  overlayer on the (100) surface of the platinum substrate. The first layer was taken to be pure copper, as was found in the experiment, while the second was a mixed copper-platinum, the third a copper and the fourth again a mixed layer. The fifth and all other layers were pure platinum. For the alloy overlayer the same potentials as for the  $\text{Cu}_3\text{Pt}$  single crystal were used, and the potential of pure platinum for the substrate.

In order to check whether the structure was correct the LEED-intensities for the (10) beam were calculated as a function of primary energy and compared with the experimental result. It was clearly found, that a four layer alloy gave the best agreement with the experimental finding. The lattice constant was taken to be intermediate between those of Pt and  $\text{Cu}_3\text{Pt}$ . Intuitively one would of course not expect the fourth layer (counted from the surface) to be ordered, but rather assume an in some way disordered transition to the substrate. Unfortunately we are not yet capable of simulating that. Whether rumpling of the first or second layer ameliorates the agreement could also not be tested. Of course we cannot evaluate the influence of a varying lattice constant as one would expect to find in a real system. The experimental [12] and theoretical results are shown in figure 4. The agreement between the two curves is not overwhelming, but encouraging when considering the complexity of the system.

With this structure the photoemission intensities of the alloy overlayer on a platinum substrate were determined. As before, the curves shown in the right panel of figure 3 are for HeI radiation impinging at different angles of incidence. The angles of electron emission are given for each curve. The agreement with the experiment (fig. 3, middle panel), which was already good, has been improved compared to the  $\text{Cu}_3\text{Pt}$  single crystal results (fig. 3, left panel): the extra intensities seen in the experimental spectra near the Fermi energy do indeed arise from a contribution of the platinum substrate. Remaining deviations between experiment and theory may have to do with differences in the exact structure in both cases.

## RESULTS FOR A $\text{Cu}_5\text{Pt}_3$ OVERLAYER ON A Pt SURFACE

After annealing the overlayer at even higher temperature a  $p(2 \times 2)$  structure was found, which was attributed to the formation of a  $\text{Cu}_5\text{Pt}_3$  overlayer [9,10]. The first layer consists, as before, of pure copper. In the second layer the unit cell consists of three platinum atoms and one copper atom, as depicted in the right panel of fig. 1. The measurements were performed with the same geometry as described above. Again, HeI radiation was used. In the calculations we assumed, as before, a configuration of four layers of the alloy on the Pt substrate (see right panel of fig. 2). Figure 5 shows the comparison between theoretical and experimental data. The positions of the peaks are again nicely reproduced. This clearly demonstrates that even for such a complicated system quantitative theoretical results are already possible. The agreement could be improved by using potentials determined for this special configuration and by optimizing the structure by comparison with experimental I-V-LEED data, which was not yet possible.

## COMPARISON BETWEEN ORDERED AND DISORDERED $\text{Cu}_3\text{Pt}$

In order to elucidate the influence of disorder on the photoemission spectra we performed calculations for a pseudo-disordered system, in that we enlarged the layer unit cell to four times the original size and distributed the atoms quasi-randomly. The curves shown in the left panel of figure 6 are for  $\text{Cu}_3\text{Pt}$ . On the right side of the figure the experimental curves for an ordered and disordered overlayer on platinum can be seen [12]. We observe a broadening in the theoretical spectrum, whereas the change in the experimental data is barely visible. The difference between the two panels may arise for several reasons: in the first place, the calculations were performed for an ordered and a disordered  $\text{Cu}_3\text{Pt}$  single crystal and not for an alloy overlayer on a substrate; secondly, when depositing a structures on top of another one must assume a region of transition. One cannot expect the  $\text{Cu}_3\text{Pt}$  overlayer to be completely ordered at its interface. Thirdly one should of course assume a change in the lattice constant from one layer to the next. This means, that in the experiment we may actually not compare a totally ordered system with a totally disordered one.

It would be interesting to compare these results with those of a CPA (coherent potential approximation) calculation. For a real test of both methods a system should be found which shows a more pronounced change when going from one phase to the other, than found for the system presented in this paper.

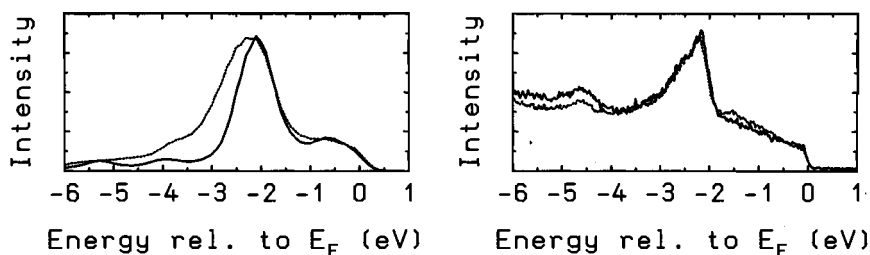


Figure 6: Theoretical and experimental results for an ordered and a disordered system: on the left theoretical data for a  $\text{Cu}_3\text{Pt}$  single crystal and on the right experimental findings for a  $\text{Cu}_3\text{Pt}$  alloy overlayer on a platinum substrate. The spectra for the ordered species are traced with continuous lines, whereas those for the disordered species are given in dotted lines. The spectra were normalized to equal peak height.

## SUMMARY

In this paper we have presented results of calculations of LEED and photoemission intensities of a  $\text{Cu}_3\text{Pt}$  single crystal, of an overlayer of  $\text{Cu}_3\text{Pt}$  geometry on an unreconstructed platinum (100) surface, of an  $\text{Cu}_5\text{Pt}_3$  overlayer on the same substrate, as well as a comparison between an ordered  $\text{Cu}_3\text{Pt}$  and a disordered  $\text{Cu}_{75}\text{Pt}_{25}$  phase. The agreement between experimental and theoretical results is generally very satisfactory, especially as the systems considered are rather complex ones. To our knowledge these are the first calculations for alloy overlayers on a substrate performed up to now.

We clearly demonstrated that, in going from a bulk  $\text{Cu}_3\text{Pt}$  to an overlayer on platinum, the influence of the substrate reflects in the photoemission spectra and that its consideration improves the agreement with the experimental data.

We also showed that the photoemission intensities of such a complex system as  $\text{Cu}_5\text{Pt}_3$  on a platinum substrate can be calculated in good agreement with experiments and this renders confidence into the power of the theoretical methods and the underlying principles.

Of course, our way to determine the photoemission spectrum of a disordered species is only one of several approaches and a comparison with a CPA calculation should be made. The implementation of the CPA method is in progress.

## ACKNOWLEDGMENTS

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# Application of a New Tight-Binding Total Energy Method to 4-d Transition Metals and Compounds

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## 1 Introduction

Since the appearance of the classic Slater-Koster (SK) paper[1] in 1954, numerous applications using the tight binding method as an interpolation scheme have been published. These works cover a wide spectrum of approaches ranging from those that aim toward simplicity by reducing the number of orbitals used, thus requiring determination of a small number of parameters, to those applications that emphasize accuracy, hence requiring a large number of parameters for implementation. The first author of this article and various collaborators have adopted the latter point of view in a series of papers including a handbook applying the SK method [2].

The scope of the early papers was to use the SK approach to accurately interpolate the results of first principles calculations of the energy bands and densities of states. An important characteristic of these calculations is that the first, second, and third nearest neighbor interactions are treated as independent parameters, which is advantageous for minimizing the rms deviation from the first principles bands.

In later years the emergence of total energy calculations and the need for SK parameters transferable from one structure to another led to the requirement that different-neighbor parameters be described by some analytical expression[3]. This linking of SK parameters and the additional requirement that the SK Hamiltonian (with, in most cases, the aid of a repulsive potential) should reproduce the ab-initio total energy, resulted in the deterioration of the fit to the original band structure. Nevertheless, the importance of obtaining the total energy in the SK scheme has been the driving force of constructing SK Hamiltonian in the '90s.

Recent papers [4-6] of the NRL group have concentrated on a tight-binding methodology that simultaneously fits the energy bands and the total energy of the fcc and bcc structures as a function of volume, and correctly predicts the ground state for those metals that crystallize in the hcp or even the  $\alpha$ -Mn structure.

In this paper we give a few examples from our work on the monatomic materials and present some new results on how our method extends to binary systems.

## 2 Theory

We write a tight-binding (TB) Hamiltonian which, in general, is non-orthogonal,

$$(\tilde{H} - \epsilon\tilde{S})\Psi = 0 \quad (1)$$

and has nine orbitals per atom (s, p and d). The matrix elements of this Hamiltonian contain the so-called Slater-Koster (SK) parameters which include on-site terms and hopping integrals. As an extension of the standard Slater-Koster approach we introduce environment-dependent parameters as follows: we write the on-site TB parameters  $h_l$  in the form of a polynomial,

$$h_l(\rho) = \alpha_l + \beta_l\rho^{2/3} + \gamma_l\rho^{4/3} + \delta_l\rho^2 \quad (2)$$

where  $l$  is an angular momentum index, and  $\rho$  measures the density of neighboring atoms,

$$\rho = \sum_{j \neq i} e^{-\lambda^2 R_{ij}}$$

where  $\lambda$ ,  $\alpha_l$ ,  $\beta_l$ ,  $\gamma_l$  and  $\delta_l$  are new parameters to be determined by fitting to first principles calculations and  $R_{ij}$  is the atoms positions. The hopping integrals have the form

$$P_i(r) = (a_i + b_i r + c_i r^2) e^{-d_i^2 r} \quad (3)$$

where  $P_i$  represents the ten SK parameters  $ss\sigma$ ,  $sp\sigma$ ,  $pp\sigma$ ,  $pp\pi$ ,  $sd\sigma$ ,  $pd\sigma$ ,  $pd\pi$ ,  $dd\sigma$ ,  $dd\pi$  and  $dd\delta$ ,  $r$  is the distance between atoms, and  $a_i$ ,  $b_i$ ,  $c_i$  and  $d_i$  are parameters to be determined by the fit. Both  $h_l$  and  $P_i(r)$  are multiplied by a cutoff function that restricts the calculation to about five shells of neighboring atoms.

A unique feature of our method is that we fit the above Hamiltonian simultaneously to the energy bands and the total energy of a given material. We write the total energy as follows:

$$E[n(r)] = \sum_{occ} \epsilon_n + F[n(r)] \quad (4)$$

where the first term represents the sum of the occupied states and  $F$  represents the remaining terms of the total energy expression that depend on the charge density  $n(r)$ .

Here we introduce a quantity,

$$V_o(S, a) = \frac{F[n(r)]}{N_e} \quad (5)$$

where  $N_e$  is the number of valence electrons. Note that  $V_o$  depends on the structure  $S$  and the lattice parameter  $a$ . The substitution (5) allows us to write the total energy according to the following sum,

$$E[n(r)] = \sum_{occ} \epsilon'_n \quad (6)$$

where  $\epsilon'_n = \epsilon_n + V_o$ .

The result is that the sum of the shifted eigenvalues is equal to the total energy and therefore we avoid the use of a pair potential needed in other formalisms.

## 3 Numerical Procedure

For the case of monatomic materials, we first perform self consistent Augmented Plane Wave (APW) calculations[7], typically for 5 different lattice constants in each of the fcc and bcc structures. The TB Hamiltonian described in the previous section is fitted to the resulting energy bands and total energies. The fitting of the energy bands is done using 89 and 55 k-points in the irreducible Brillouin zone for fcc and bcc respectively. We note that we fit at least six bands even if they are not all occupied and we block-diagonalize the Hamiltonian in order to avoid mismatching of different symmetries[2]. The total energy is fitted with a weight typically 300 times larger than that of the individual eigenvalues. We also restrict the behavior of the hopping integrals in Eq. 3 so that they are

decreasing functions of distance and do not change sign. The number of parameters in Eqs. 2 and 3 are, for a non-orthogonal Hamiltonian, 97 and 306 for monatomic and diatomic materials respectively. For an orthogonal Hamiltonian, the number of parameters are 57 and 136 respectively. It is important to state our philosophy about the large number of parameters involved in the fitting. We remind the reader that we do not fit to experiment but to first-principles calculation and therefore these parameters should be viewed as intermediate quantities in changing the APW basis set to a tight-binding (i.e., linear combination of atomic orbitals) representation. In practice for most monatomic

Table 1: Relative energies per atom of several structures for each of the metals examined by the tight-binding model discussed in the text. The energy of the experimental ground state structure is arbitrarily set to zero. All energies are calculated at the equilibrium volume found by the tight-binding fit, and are expressed in mRy. Below the common name of each phase is its *Strukturbericht* designation.

| Element | Structure |           |           |               |                      |            |
|---------|-----------|-----------|-----------|---------------|----------------------|------------|
|         | fcc<br>A1 | bcc<br>A2 | hcp<br>A3 | diamond<br>A4 | sc<br>A <sub>h</sub> | αMn<br>A12 |
| Sr      | 0.0       | 2.1       | 1.0       | 73.0          | 22.0                 | 3.2        |
| Y       | 2.4       | 8.8       | 0.0       | 97.9          | 432.2                | 8.6        |
| Zr      | 1.1       | 2.9       | 0.0       | 112.7         | 123.3                | 8.6        |
| Nb      | 26.1      | 0.0       | 22.7      | 181.9         | 68.6                 | 17.1       |
| Mo      | 30.0      | 0.0       | 31.0      | 147.3         | 68.7                 | 17.5       |
| Tc      | 6.1       | 23.3      | 0.0       | 72.9          | 56.3                 | 0.2        |
| Ru      | 1.0       | 44.6      | 0.0       | 134.5         | 106.6                | 16.3       |
| Rh      | 0.0       | 31.7      | 5.1       | 159.8         | 96.0                 | 16.3       |
| Pd      | 0.0       | 9.9       | 2.5       | 148.6         | 84.9                 | 9.2        |
| Ag      | 0.0       | 3.3       | 0.6       | 66.1          | 24.1                 | 6.0        |

Table 2: Elastic constants and bulk moduli for 4d cubic elements. Comparison is made between the results of our tight-binding parametrization (TB), first-principles full potential LAPW results (LAPW), where available, and experiment (Exp.). Calculations were performed at the experimental volume.

|    | $C_{11}$ |      |     | $C_{12}$ |      |     | $C_{44}$ |      |     | $B_0(\text{GPa})$ |      |     |
|----|----------|------|-----|----------|------|-----|----------|------|-----|-------------------|------|-----|
|    | TB       | LAPW | Exp | TB       | LAPW | Exp | TB       | LAPW | Exp | TB                | LAPW | Exp |
| Sr | 8        |      | 15  | 3        |      | 6   | -3       |      | 10  | 15                |      | 12  |
| Nb | 204      | 230  | 246 | 137      | 122  | 139 | 34       | 25   | 29  | 187               | 193  | 170 |
| Mo | 453      | 468  | 450 | 147      | 149  | 173 | 120      | 98   | 125 | 283               | 291  | 272 |
| Rh | 491      | 433  | 413 | 171      | 185  | 194 | 260      | 206  | 184 | 306               | 309  | 272 |
| Pd | 233      | 218  | 227 | 163      | 172  | 176 | 63       | 74   | 72  | 212               | 220  | 181 |
| Ag | 133      | 122  | 124 | 86       | 90   | 93  | 42       | 52   | 46  | 142               | 142  | 101 |

Table 3: Elastic constants and bulk moduli for hexagonal close-packed elements. Comparison is made between the results of our tight-binding parametrization (TB) and experiment (Exp). The tight-binding results include internal relaxation. Calculations were performed at the experimental volume, but at the  $c/a$  ratio which minimized the energy for that volume. Note that in a hexagonal crystal,  $C_{66} = (C_{11} - C_{12})/2$ .

|    | $C_{11}$ |     | $C_{12}$ |     | $C_{13}$ |     | $C_{33}$ |     | $C_{44}$ |     | $B_0(\text{GPa})$ |     |
|----|----------|-----|----------|-----|----------|-----|----------|-----|----------|-----|-------------------|-----|
|    | TB       | Exp | TB       | Exp | TB       | Exp | TB       | Exp | TB       | Exp | TB                | Exp |
| Y  | 45       | 78  | 15       | 29  | 13       | 20  | 48       | 77  | 17       | 24  | 46                | 37  |
| Zr | 102      | 144 | 67       | 74  | 65       | 67  | 99       | 166 | 4        | 33  | 108               | 83  |
| Tc | 477      |     | 196      |     | 172      | 505 |          | 127 |          |     | 304               | 297 |
| Ru | 642      | 563 | 170      | 188 | 129      | 168 | 706      | 624 | 214      | 181 | 360               | 321 |



Table 4: Tight-binding vacancy formation energies compared to first-principles calculations and experiment. Energies were computed using a 108 atom supercell. The experimental column shows a range of energies if several experiments have been tabulated. Otherwise the estimated error in the experiment is given.

| Element | Vacancy Formation Energy (eV) |         |                 |
|---------|-------------------------------|---------|-----------------|
|         | Tight-Binding                 |         | Experiment      |
|         | Fixed                         | Relaxed |                 |
| Nb      | 2.84                          | 2.82    | $2.65 \pm 0.3$  |
| Mo      | 2.63                          | 2.46    | 3.0 - 3.6       |
| Rh      | 3.39                          | 3.35    | 1.71            |
| Pd      | 2.46                          | 2.45    | $1.85 \pm 0.25$ |
| Ag      | 1.31                          | 1.24    | 1.11 - 1.31     |

materials we have omitted the quadratic term in Eq. 3, thus reducing the number of parameters. Also, in many cases we exclude certain orbitals which would lead to further reduction of the number of parameters. For example, in C or NbC it is reasonable to omit the C d-orbitals. For monatomic materials our fitting rms error is about 5 mRy for the bands and 0.5 mRy for the total energies. For diatomic materials our rms error for the bands is much larger ranging from 20 mRy to 50 mRy and for the total energy about 1 mRy.

### 4 Results

In the bibliography the reader can find some of our recent papers for a complete account of our results. In this paper we present some representative results as follows :  
In table 1 we give the relative energy per atom for 6 different structures in the second row of the transition metals. The fit was performed only for fcc and bcc structures to the APW results, and therefore the other structures are found as output of our TB scheme. Note that in every case we obtain the correct ground state, i.e. the elements Y, Zr, Tc and Ru are predicted correctly to be hcp without having included this structure in the fit.

Table 5: Surface energies, calculated from the tight-binding theory (TB), by the embedded-atom method (EAM), or by modified embedded atom method (MEAM), compared to experiment. Energies are given in units of J/m<sup>2</sup>.

| Element | Orientation | TB   | EAM  | MEAM | Experiment |
|---------|-------------|------|------|------|------------|
| Nb      | (111)       | 2.44 |      | 2.02 | 2.3        |
|         | (110)       | 1.54 | 1.81 | 1.87 |            |
|         | (100)       | 2.37 | 1.97 | 2.02 |            |
| Mo      | (111)       | 2.84 |      | 1.86 | 2.9        |
|         | (110)       | 3.04 | 2.13 | 1.93 |            |
|         | (100)       | 2.12 | 2.28 | 2.12 |            |
| Rh      | (111)       | 2.46 |      | 2.60 | 2.60       |
|         | (110)       | 2.71 |      | 2.92 |            |
|         | (100)       | 2.57 |      | 2.90 |            |
| Pd      | (111)       | 1.57 | 1.22 | 1.38 | 2.00       |
|         | (110)       | 1.86 | 1.49 | 1.67 |            |
|         | (100)       | 1.75 | 1.37 | 1.66 |            |
| Ag      | (111)       | 1.14 | 0.62 | 1.09 | 1.32       |
|         | (110)       | 1.42 | 0.77 | 1.27 |            |
|         | (100)       | 1.29 | 0.71 | 1.22 |            |

In table 2 and 3 we present our results for the elastic constants and bulk moduli of the above metals and compare with experiment and first-principles calculations. The elastic constants are calculated by imposing an external strain on the crystal, relaxing any internal parameters (case of hcp crystals) to obtain the energy as a function of the strain[8]. These calculations are also an output of our TB approach, and especially for the hcp materials, they would be very costly to be performed from first-principles. For the cubic materials the elastic constants are consistent with the LAPW values and are to within 15% of experiment. This is the accepted standard of comparison between first-principles calculations and experiment. An exception is Sr which has a very soft lattice and the accurate determination of elastic constants is problematic. For the hcp materials our results are less accurate and specifically in Zr the  $C_{44}$  is seriously underestimated .

Another application of our TB method is in the calculation of vacancy formation energies. Calculations with the atoms at the primitive lattice sites in the crystal (Fixed) and allowing relaxation around the vacancy (Relaxed) are shown. The results are summarized in table 4. Again we have good accord between theory and experiment, with the notable exception of Rh whose vacancy energy is overestimated by the TB scheme. It is worth noting that the experimental trend that the bcc energies are larger than those for the fcc metals is also found in our calculations. These calculations involve 108 atoms in a supercell. Such calculations, even on supercomputers, are very slow using first-principles methods. Typically an APW calculation with 100 atoms would be two orders of magnitude slower than the corresponding TB calculations.

In table 5 we present results of our TB methodology for surface energies comparing them to experiment, and atomistic models. The surface energy is expressed as the energy required to create a unit area of new surface, and is given by the following formula :

$$E_{surf} = \frac{1}{2A}(E_{slab} - N E_{bulk})$$

where A is the area occupied by one unit cell on the surface of the slab,  $E_{slab}$  is the total energy of the slab, N is the number of atoms in the unit cell, and  $E_{bulk}$  is the energy of one atom in the bulk at the lattice constant of the atoms in the interior of the slab[6]. These calculations were performed using a slab containing 25 atoms per unit cell. Our results for fcc metals conform to the relationship  $E_{111} < E_{100} < E_{110}$ , which shows that the close packed surfaces are most stable for fcc metals. The TB surface energies are uniformly larger, and closer to experiment, than those obtained by the embedded atom method(EAM), which is known to underestimate surface energies in fcc metals. For the bcc metals our results are also good, for all unrelaxed surfaces we found  $E_{110} < E_{100} < E_{111}$ , and energies closer to experimental results than those obtained by the modified embedded atom method (MEAM).

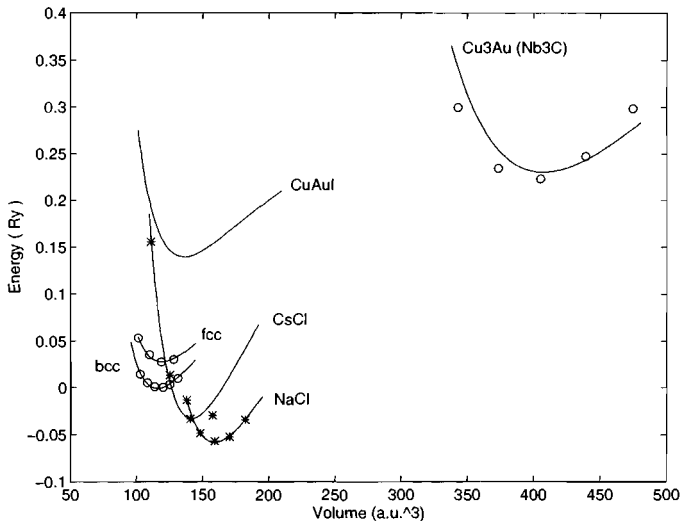


Figure 1: Formation energy as a function of volume for NbC

We have also used our method to study grain boundaries, which play an important role in determining the properties of metals[9]. Since these structures involve large number of atoms in the unit cell, calculation of grain boundary formation energies cannot be easily performed using first-principles calculations. We have used the tight-binding method to determine the formation energy of two twin boundaries in Niobium,  $\Sigma = 5[001](210)$  and  $\Sigma = 5[001](310)$ . These calculations were done by periodically replicating the grain boundary in the  $[2\ 1\ 0]$  and  $[3\ 1\ 0]$  directions respectively. The atoms were kept at their bulk positions except near the grain boundary, where the layer spacing was adjusted so that the nearest neighbor distance was the same as in the bulk, thus our calculations yield an upper bound on the energy needed to form the boundaries. In both cases a supercell containing 40 atoms was large enough to eliminate the interaction between repeated twin boundaries. For the  $\Sigma = 5[001](210)$  boundary we find a formation energy of  $2.3\text{ J/m}^2$ , while for the  $\Sigma = 5[001](310)$  boundary we find  $2.0\text{ J/m}^2$ . This latter value should be compared to the embedded atom model calculation of Farkas[10], who found an energy of  $1.7\text{ J/m}^2$  for the unrelaxed cell. Since EAM calculations often underestimate energies at surfaces, it is not surprising that this energy is some what lower than ours.

At present we are extending this methodology to binary compounds. An example of our results is shown in Fig.1 . This shows a phase diagram for NbC that includes the NaCl, CsCl, CuAuI, Cu<sub>3</sub>Au, and pure Nb fcc and bcc structures. The solid lines indicate the TB formation energy , the open circles and asterisks are the APW energies to which we fitted. We should emphasize that CuAuI and Cu<sub>3</sub>Au structures are an output of our TB scheme and were not fitted. In the case of Cu<sub>3</sub>Au structure we performed APW calculations and it can be seen that the TB scheme fits well the APW results. We have also calculated elastic constants for NbC and although they predict the stability of the NaCl structure they are less accurate than those we found for monatomic materials. For the binary case our preliminary results for NbC and a few other binary systems that we tested suggest that this approach will also be successful but with considerably more effort in the least-square fitting step of determining the TB parameters.

## 5 Summary

We presented selected results from a new tight-binding total energy method that accurately predicts ground state properties of transition and noble metals, and successfully extended to transition metal carbides.

## 6 Acknowledgments

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# STUDY OF MAGNETIC CLUSTERS USING A TIGHT BINDING MOLECULAR DYNAMICS APPROACH

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## ABSTRACT

The tight-binding molecular-dynamics (TBMD) method has been proved to be a useful tool in the study of semiconductors. Recently, we extended this method to the study of transition metal systems. Our applications to non-magnetic clusters of transition metal atoms gave results for the binding energies, bond lengths and vibration frequencies of  $\text{Ni}_n$  clusters ( $n$  upto 55) in very good agreement with both theory and experiment. In the present work we extend the applicability of the formalism to include the study of magnetic properties of the  $\text{Ni}_n$ ,  $\text{Fe}_n$  and  $\text{Co}_n$  clusters ( $n \leq 55$ ). This is achieved by incorporating an exchange splitting term in the TBMD Hamiltonian. It is shown that the results obtained for the magnetic moment (per atom) for Ni, Fe and Co clusters are in very good agreement with recent experimental data, thus establishing the validity of our scheme in the treatment of magnetic systems and/or their alloys.

## INTRODUCTION

Recent experimental results<sup>1,2</sup> have indicated exceedingly high magnetization in small free ferromagnetic clusters of  $\text{Fe}_n$ ,  $\text{Ni}_n$  and  $\text{Co}_n$ . The values of the average magnetic moment,  $\bar{\mu}_n$ , per atom of a cluster consisting of  $n$ -atoms, were found to decrease with an increase in the cluster size (i.e. the number of atoms in the cluster), approaching the corresponding bulk values for large enough  $n$  ( $n \approx 500$ -700 atoms). This decrease, however, is found to be not monotonic. Deviations of  $\bar{\mu}_n$  from its monotonic decrease have been attributed to surface effects; clusters consisting of closed icosahedral structures (like  $\text{Ni}_{13}$ ,  $\text{Ni}_{33}$  and  $\text{Ni}_{55}$ ) were found to exhibit considerably low values of magnetic moments when compared to those with open structures<sup>2</sup>. Accurate theoretical calculations

on small clusters have also shown that small ferromagnetic clusters exhibit enhanced magnetization, much larger than their corresponding bulk material. Challenge has been posed to the theory to give a quantitative description of the experimental findings and provide an answer to the critical question of how the magnetic ordering affects the geometry of the cluster and vice versa.

Various theoretical approaches that have been used so far<sup>3-15</sup> have indicated the difficulties associated with these problems and have shown that the magnetic behavior of small ferromagnetic clusters is the outcome of a very delicate interplay among various factors such as the kind of atoms (filling of the d-band), size of the cluster, bond lengths and coordination numbers, as well as the symmetry of the cluster. Each of these factors represent an independent variable of the total energy of the cluster and in the search for the true ground state of the cluster it is necessary to minimize its total energy with respect to a simultaneous variations of all these variables. Thus, the quantitative description of the properties of the magnetic clusters is a very difficult computational problem. As a consequence, while the *ab initio* calculations<sup>3-6,14,15</sup> are restricted to very small clusters, ( $n \leq 7$ ), the results reported for larger clusters ( $n > 7$ ) involve total energy optimizations that use severe constraints in one or more of the independent parameters of the system<sup>7,10-13</sup>. Among the constraints employed to expedite the calculations the most severe is the one restricting its geometry (symmetry). Furthermore, model approximations, (e.g., the neglect of the  $s - d$  interactions in a tight-binding description) seem to introduce significant errors.

In the present work, we report on a new semi-empirical theoretical approach which allows us to perform spin and symmetry unconstrained total energy calculations for clusters of transition metal atoms in a computationally efficient way. Our approach is based on the Tight Binding Molecular Dynamics (TBMD) method.

In the following, we give a brief review of the method and then we present applications to Ni, Fe and Co magnetic clusters.

## COMPUTATIONAL APPROACH

Recently, we extended the applicability of the TBMD method, that has been used very successfully in the studies of semiconductors<sup>18</sup> to study clusters of transition metal atoms. We have shown<sup>19-21</sup> that TBMD successfully describes the clusters of transition metal atoms, giving results for the cluster geometries, vibration frequencies and magnetic moments in very good agreement with both theory<sup>3-7,19,11</sup> and experiment<sup>16,17,1,2</sup>. The detailed description of our method and its accuracy have been given elsewhere<sup>19,20</sup>. Briefly, our method makes use of the universal tight binding parameters of Harrison<sup>22</sup>, scaled exponentially with respect to the inter-atomic distance, and employs a minimal set of five parameters obtained by fitting to theoretical and experimental data. These include the experimental or theoretical bond length of the dimer, the average strength of the exchange splitting and the *ab initio* results of the total energy of three small clusters. For the dimers Ni<sub>2</sub> and Fe<sub>2</sub>, we used the experimental bond lengths, i.e. 2.20 Å and 2.02 Å, respectively. For the Co<sub>2</sub> dimer, we used the theoretical value of the bond length, i.e. 2.43 Å. The *ab initio* total energy data for small clusters allow us to calibrate the energy correction term,  $U_{bond}$ , which depends on the number of bonds per atom, originally introduced by Tomanek and Schluter<sup>23</sup>. On the other hand, the fitting to the experimental bond length of the dimer allows us to determine the coefficient of the pair-wise repulsive interaction term which also includes a correction to the double counting of the electron-electron interactions in the total energy<sup>18,19</sup>. Finally, by fitting to the total energy of various spin states of small clusters, we are able to estimate the

**Table I.** Results for the average magnetic moment per atom,  $\bar{\mu}_n$ , (in Bohr magnetons,  $\mu_B$ ) and binding energies,  $\bar{E}_n$ , (in eV/atom) for various  $Ni_n$  clusters, as obtained by using the TBMD method, are compared with available experimental data. The experimental results are deduced from references 1 and 2, and have been re expressed using a gyromagnetic constant of  $g=2.0$ . The geometries, in general, are slightly distorted from the ideal symmetric configurations.

| Cluster          | Symmetry             | $\bar{\mu}_n$ |            |           | $\bar{E}_n$ |
|------------------|----------------------|---------------|------------|-----------|-------------|
|                  |                      | Present       | exp. Ref.2 | exp.Ref.1 | Present     |
| Ni <sub>5</sub>  | Trig.Bipyr.          | 1.600         | 1.81       |           | 2.431       |
|                  | Trig.Bipyr.          | 1.200         |            |           | 2.352       |
| Ni <sub>6</sub>  | C <sub>4v</sub>      | 1.333         | 1.47       |           | 2.603       |
|                  | C <sub>4v</sub>      | 1.667         |            |           | 2.590       |
|                  | C <sub>4v</sub>      | 2.000         |            |           | 2.598       |
| Ni <sub>7</sub>  | C <sub>5v</sub>      | 1.143         | 1.53       |           | 2.760       |
|                  | C <sub>5v</sub>      | 1.429         |            |           | 2.683       |
|                  | C <sub>5v</sub>      | 1.714         |            |           | 2.657       |
| Ni <sub>8</sub>  | capped<br>squar.pyr. | 1.250         | 1.58       |           | 2.997       |
|                  | "_"                  | 1.500         |            |           | 2.992       |
| Ni <sub>13</sub> | capped anti-prism    | 1.077         | 0.96       |           | 3.259       |
|                  | "_"                  | 1.231         |            |           | 3.261       |
|                  | "_"                  | 1.385         |            |           | 3.233       |
| Ni <sub>23</sub> | fcc                  | 0.870         | 1.20       | 0.95      | 3.694       |
|                  | fcc                  | 1.043         |            |           | 3.701       |
| Ni <sub>33</sub> | icos-twin            | 0.848         | 1.02       | 0.94      | 4.090       |
|                  | "_"                  | 0.909         |            |           | 4.082       |
| Ni <sub>43</sub> | fcc                  | 0.930         | 1.14       | 0.85      | 4.080       |
|                  | fcc                  | 1.070         |            |           | 4.077       |
| Ni <sub>44</sub> | fcc                  | 0.864         | 1.01       |           | 4.208       |
| Ni <sub>55</sub> | icos                 | 1.018         | 0.93       | 0.76      | 4.545       |
|                  | icos                 | 0.873         |            |           | 4.544       |
|                  | fcc                  | 0.836         |            |           | 4.340       |

average strength of the exchange splitting<sup>20</sup>. Following the methodology described in reference 20, we find the average exchange splitting for Ni, Fe and Co , compatible with the higher spin states of their small clusters, to be 0.90, 2.10 and 1.10 eV respectively.

### RESULTS AND CONCLUSIONS

In this section, we compare our results for the magnetic moments of  $Ni_n$ ,  $Fe_n$  and  $Co_n$ ,  $n \leq 55$ , clusters with available experimental data. We point out that the determination of the exact ground state of these clusters is a very difficult task because these clusters exhibit a number of various spin states with energies lying very close to the ground state and within the range of both the calculational and the experimental errors.

Our results are included in Tables I and II along with available experimental data for comparison. For Ni, calculations were performed by including the coordination dependent energy term,  $U_{bond}$ . This was facilitated by the availability of necessary *ab*

**Table II.** Results for  $\text{Fe}_n$  and  $\text{Co}_n$  clusters as in Table I.

| Cluster          | Symmetry | $\bar{\mu}_n$ |           | $E_n$   |
|------------------|----------|---------------|-----------|---------|
|                  |          | Present       | exp.Ref.1 | Present |
| $\text{Fe}_{27}$ | bcc      | 2.667         | 2.84      | 8.209   |
|                  | bcc      | 2.518         |           | 8.243   |
| $\text{Fe}_{55}$ | icos     | 2.473         | 2.95      | 8.678   |
|                  | icos     | 2.764         |           | 8.644   |
|                  | fcc      | 3.055         |           | 8.545   |
|                  | fcc      | 2.691         |           | 8.656   |
| $\text{Co}_{43}$ | fcc      | 1.791         | 2.01      | 3.995   |
|                  | fcc      | 1.950         |           | 3.993   |
|                  | fcc      | 2.023         |           | 3.986   |
| $\text{Co}_{55}$ | icos     | 1.909         | 1.92      | 4.139   |
|                  | fcc      | 1.800         |           | 4.097   |

*initio* data for the calibration of this term. In the case of Fe and Co, the unavailability of sufficient *ab initio* results precludes an accurate calibration of this term and, therefore, no use is made of this term for obtaining the results presented in Table II for Fe and Co.

Our optimized cluster geometries agree well with other reported results for most part. One noticeable exception, however, is the case of  $\text{Ni}_{13}$  for which we find a capped distorted trigonal anti-prism structure with a central atom to be the most stable geometry<sup>21</sup>, while the previously proposed distorted icosahedral structure<sup>13</sup> was found to be unstable. We note that no full geometry unrestricted Optimization was done in obtaining the structure of Ref.13.

In Fig. 1, the stable geometry of the true ground state (capped distorted trigonal anti-prism) of  $\text{Ni}_{13}$  is shown. This structure has a central atom and the overall coordination for this cluster is lower than in the fcc or distorted icosahedral geometry. In view of this magnetic effects induced evolution of the ground state geometry of  $\text{Ni}_{13}$ , we considered similar possibilities for  $\text{Ni}_{12}$  and  $\text{Ni}_{14}$ . Interestingly, the magnetic ground state of  $\text{Ni}_{12}$  is also obtained to be a capped distorted trigonal anti-prism, but with no central atom (Fig. 1). The ground state geometry of  $\text{Ni}_{14}$ , however, is found to be a capped square pyramid with a central atom (Fig. 1). This structure, in addition to having atoms cap its sides, also has a capping atom at its top. Both the ground states of  $\text{Ni}_{12}$  and  $\text{Ni}_{14}$  contain Ni atoms with lower coordination than the corresponding fcc or icosahedral like structures. These observations lead us to believe that the main effects of magnetism in small Ni clusters is to drive their evolution from fcc or icosahedral to capped prism or anti-prism geometries with lower coordination for Ni atoms.

In general, we find<sup>19</sup> that for the singlet states of the clusters when cluster size is such that closed icosahedral geometry is possible, this structure appears to be more stable than the fcc, bcc or hcp ones, in agreement with the experimental findings<sup>16,17</sup>. For the higher spin states, however, we find that the relaxed geometries are either less distorted or exhibit higher symmetries when compared with their singlet counterpart<sup>20</sup>, in agreement with Dunlap's conjecture<sup>10</sup>. It is clear from the results presented in Tables I and II that our calculated magnetic moments are in very good agreement with both theory<sup>3-7,12-15</sup> and experiment<sup>1,2</sup>. The observed deviations between our results and experiment are, in most of the cases, within the experimental and calculational errors, the latter being due to uncertainties associated with the estimation of the  $U_{\text{bond}}$  term,



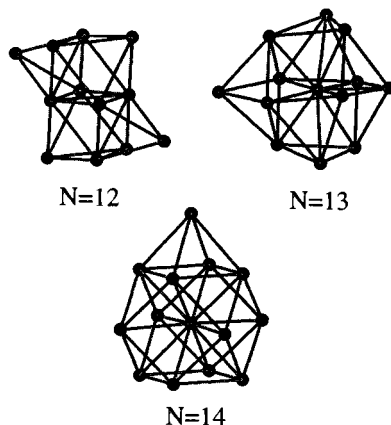


Figure 1: Ground state geometries of  $Ni_{12}$ ,  $Ni_{13}$  and,  $Ni_{14}$

the existence of many almost isoenergetic spin states of the clusters and temperature effects that have been ignored in our calculations.

The conclusions drawn from the results presented in Tables I and II can be summarized as follows :

- (i) Our TBMD approach can successfully describe the geometry and the electronic structure of the clusters of transition metal atoms and can provide quantitative results for their magnetic states as well.
- (ii) The existing experimental data are limited and do not agree among themselves for the entire range of cluster sizes.
- (iii) The apparent deviations of the calculated magnetic moments from their corresponding experimental values may be attributed to calculational uncertainties and the existence (for each cluster) of various spin states whose energies are close to the ground state energy and within the range of the thermal energy of the clusters at the experimental temperatures (for Ni, 73-198K, according to ref.2, and 78K according to ref.1; for Co 78K and for Fe 120K (ref.1)).
- (iv) The effects due to the temperature, the magnetic anisotropy and a possible small change (decrease) of the strength of the average exchange splitting as the cluster size increases, have been ignored in our analysis. Their consideration, although not expected to change the present results appreciably, however, will be helpful toward a better evaluation of the present status of theory and experimental information.

## ACKNOWLEDGMENTS

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## **ELECTRICAL CONDUCTIVITY OF INHOMOGENEOUS SYSTEMS: APPLICATION TO MAGNETIC MULTILAYERS AND GIANT MAGNETORESISTANCE**

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### **GIANT MAGNETORESISTANCE**

Recently there has been great interest in the transport properties of layered magnetic materials because of the discovery of a new form of magnetoresistance<sup>1</sup> called the giant magnetoresistance (GMR). GMR is a change in the electrical resistivity of a magnetically inhomogeneous material that occurs when the application of a magnetic field brings the moments in different regions into alignment. GMR has been observed in several geometries, but the most promising and interesting GMR systems are composed of thin layers of ferromagnetic material separated by non-magnetic or very weakly magnetic spacer layers. For layered GMR systems, electric fields are usually applied so that the current flows parallel to the layers. This "current in the plane" geometry will be assumed in this paper.

The GMR effect can be applied to make extremely small and sensitive devices for detecting magnetic fields. Such devices have many potential uses. Currently, they are being used as read sensors in prototype heads for computer disk drives. Their small size and high sensitivity are very well suited for sensing the very small changes in magnetic field associated with the small magnetized regions on a disk which store the information.

A second potential application of GMR is to magnetic random access memory devices. In these devices, information is stored as the direction of the magnetization in a small region or cell of a very thin magnetic film. The GMR effect can be used to sense this magnetization direction and determine whether a one or a zero is stored in a particular cell. More generally, GMR based devices can be used wherever there is a need to detect magnetic fields or changes in magnetic fields simply and inexpensively, e.g. position and motion sensing.

Two recent review articles<sup>2,3</sup> provide a helpful introduction to the literature on GMR.

## NON-LOCAL MECHANISM FOR GMR

Two mechanisms which contribute to GMR have been identified, a "non-local" mechanism<sup>4</sup> and a "quantum" mechanism<sup>5</sup>. To understand the first or non-local, mechanism it is necessary to understand that on the scale of the electron mean free path (possibly 10 to 20 nanometers at room temperature) electrical conduction is a non-local phenomenon. Electrons may be accelerated by an electric field in one region and contribute to the current in other regions. To a good approximation they may be viewed as contributing to the current until they are scattered.

The first mechanism is illustrated by Figures 1 to 4. These figures show the calculated non-local conductivity of a system consisting of 10 atomic layers of copper sandwiched between 11 atomic layers of cobalt on either side. The electric field is applied parallel to the planes which causes the current to flow parallel to the planes as well. The figures show the non-local layer dependent conductivity,  $\sigma^s(I,J)$ , which is the current of spin  $s$  electrons induced in atomic layer  $I$  by an electric field applied to layer  $J$ .

To a good approximation one can assume that there are two independent groups of electrons (or channels) which carry the current, majority (or spin up) and minority (or spin down). Relativistic effects can couple the electron's spin to its motion through the lattice, but this effect is usually small for the transition metals and has not been included in the calculations shown here.

For the particular calculations shown in Figures 1 - 4, it was assumed that the scattering rates are relatively high and that they are the same for all layers and for both spin channels. Both the field and the current are assumed to be parallel to the layers which consist of {111} atomic planes.

Figure 1 shows the majority conductivity,  $\sigma^{\uparrow}(I,J)$ , and Figure 2, the minority conductivity,  $\sigma^{\downarrow}(I,J)$ , for the case in which the moments in the two cobalt layers are aligned. The total conductivity for parallel cobalt moments will be the sum of the conductivities shown in Figures 1 and 2.

Note that because of the different electronic structure for majority and minority Co, the nature of the non-local conductivity is different in the two spin channels. For majority Co, the electronic structure is rather similar to that in Cu, but for minority Co, most of the Fermi energy electrons have low velocities which lead to short mean free paths and hence to localized conductivities, *i.e.* a strong peak for  $I=J$  and a rapid decrease in the conductivity as a function of  $|I-J|$ .

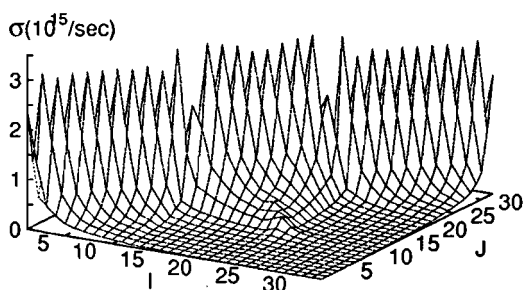


**Figure 1** Non-local layer dependent conductivity for majority electrons for parallel alignment of the cobalt moments. The scattering rate is assumed to be high so that the electron lifetime is relatively short ( $4.8 \times 10^{-13}$  sec).

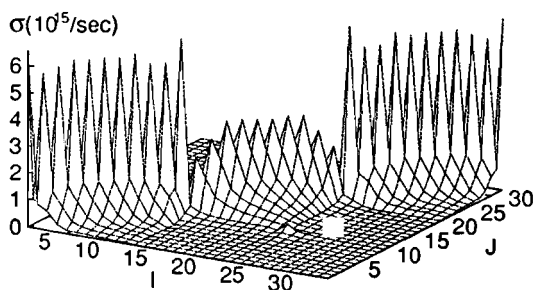


**Figure 2** Non-local layer dependent conductivity for minority electrons for parallel alignment of the cobalt moments. The scattering rate is assumed to be the same as for the majority electrons (Figure 1).

Figure 3 shows the calculated conductivity for one of the channels when the cobalt moments on either side of the copper layer are aligned anti-parallel. The spin channel for which the conductivity is shown in Figure 3 is locally the majority channel in the cobalt layer to the left of the copper (spin parallel to the Co moment) and locally minority to the right of the copper (electron spin anti-parallel to the local Co moments). The non-local conductivity for the other spin channel for the case in which the cobalt moments are anti-parallel is the mirror image of the conductivity shown in Figure 3.

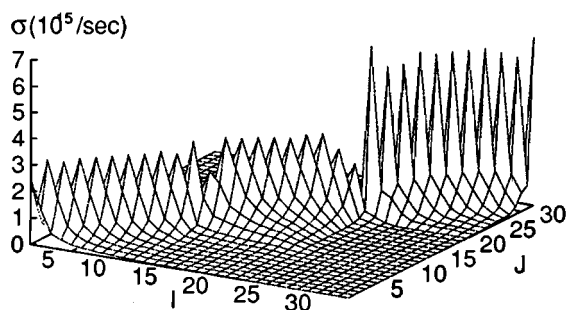


**Figure 3** Non-local layer dependent conductivity for one spin channel for anti-parallel alignment of the cobalt moments. This spin channel is locally the majority in the cobalt on the left side of the sample.

Note that majority electrons that are accelerated by the electric field in one of the cobalt layers contribute to the current, not only in that layer ( $I = J$ ) but in other layers as well, including the copper layers and the cobalt layers on the other side of the copper. On the other hand, minority electrons that are accelerated by a field in one of the cobalt layers contribute very little to the conductivity in the copper or in the cobalt on the other side of the copper. For anti-parallel alignment of the moments, electrons that are accelerated by the field in one cobalt layer contribute to the current in that layer and in the cobalt, but not in the other cobalt layer. The difference in the *total* current due to both channels between parallel and anti-parallel alignment is almost entirely non-local. It comes from those electrons that are accelerated by the applied electric field in one cobalt layer and propagate across the copper to the other cobalt layer where they contribute to the current. It is clear from Figures 1-4 that this process occurs primarily for majority electrons and for the case of parallel alignment.

The non-local nature of the contributions to the GMR can be seen in Figure 4 which shows the difference in the total non-local conductivity between the cases of parallel and anti-parallel alignment of the cobalt moments. Thus Figure 4 shows the sum of the conductivities in Figures 1 and 2 minus the sum of the conductivities in Figure 3 and its mirror image. Note that the contributions to  $\Delta\sigma$  are entirely non-local.

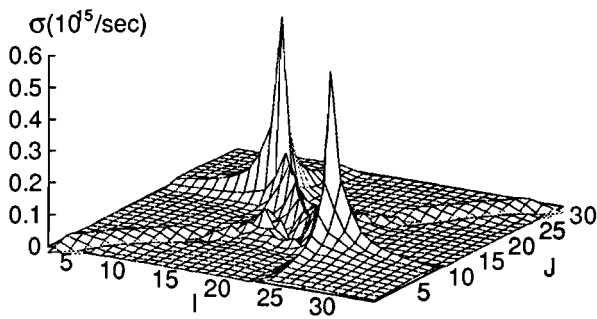


**Figure 4 Giant Magnetoconductance.** The change in the non-local layer dependent conductivity between parallel and anti-parallel alignment of the cobalt moments. For this case of strong scattering in both the cobalt and copper, contributions to the GMR come from electrons that are accelerated in one cobalt layer and contribute to the current in the other.

### QUANTUM OR WAVE GUIDE MECHANISM

The second mechanism that has been identified as a cause of GMR is a quantum or wave guide effect<sup>5</sup>. This mechanism originates in the wave nature of the electrons. Figures 5-8 show the calculated non-local conductivity for a geometry similar to that of Figures 1-4. In Figures 5-8, however, the scattering rates are chosen to be consistent with the experimentally determined resistivities of copper and cobalt. The scattering rates were chosen to be the same in both spin channels. These scattering rates are significantly lower than those of Figures 1-4 and the scattering rate in the copper is much less than in the cobalt. The lower scattering rates at the interfaces and the lower scattering rate in the copper accentuate the quantum or wave guide effect.

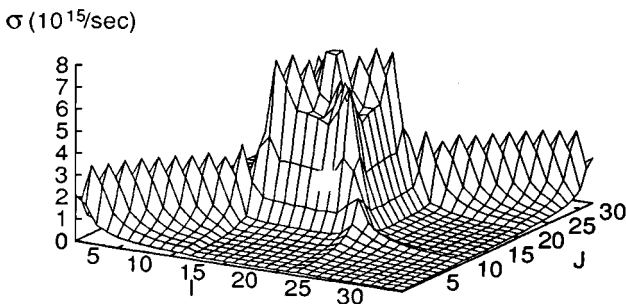


**Figure 5 Non-local layer dependent conductivity for majority electrons.**

Figures 5 and 6 show  $\sigma^{\uparrow}(I,J)$ , and  $\sigma^{\downarrow}(I,J)$ , respectively, for the case in which the cobalt moments are in parallel alignment. Figure 7 shows the non-local conductivity for anti-parallel alignment of the cobalt moments. Figure 8 shows,  $\Delta\sigma$ , the difference between the sum of the conductivities in Figures 5 and 6 and the sum of the conductivity in Figure 7 and its mirror image.

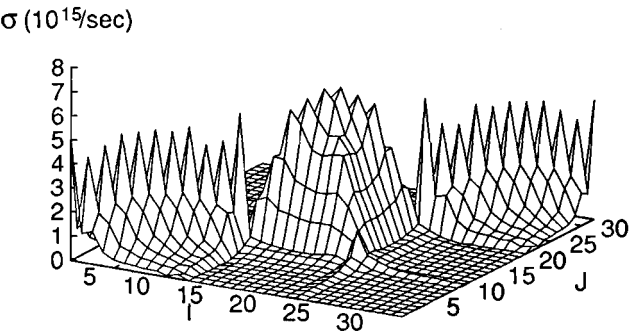


Figure 6 Non-local layer dependent conductivity for minority electrons

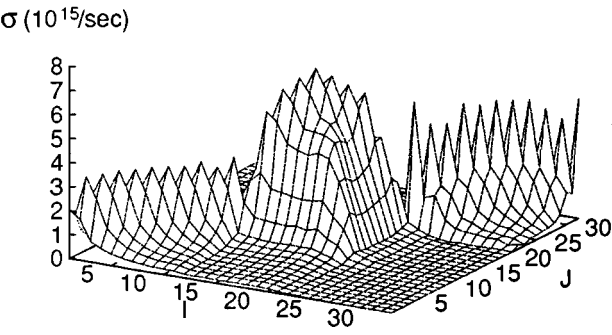


Figure 7 Non-local layer dependent conductivity for one of the channels for anti-parallel alignment of the cobalt spins.



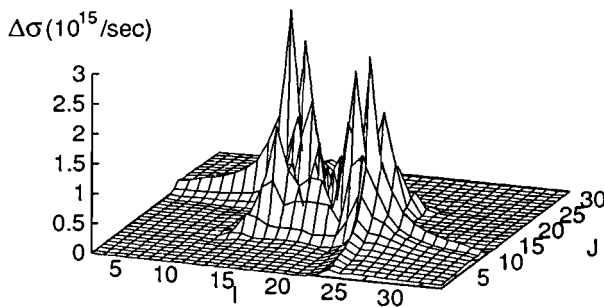


**Figure 8 Giant Magnetoconductance.** In addition to the non-local contribution seen in Figure 4, there is a contribution that appears in the copper layer that originates in the wave guide effect.

From Figure 8 it is clear that, in addition to the non-local contribution to the GMR, there is a contribution that is localized in the copper layer. The majority conductivity, shown in Figure 5, also has a very large conductivity that is localized in the copper layer. The large majority conductivity on the copper layer and the large contribution to the GMR from the copper layer originates from a wave guide effect that can be understood by examining the Fermi surfaces of copper and cobalt.

Figure 9 shows the majority Fermi surfaces of copper and cobalt. It is clear from Figure 9 that for some large values of  $k_{||}$  there are allowed values of  $k_{\perp}$  in the copper but not in the cobalt. For the minority channel, however, there is always an allowed value of  $k_{\perp}$  in the cobalt if there is an allowed value in the copper. This means that some of the majority electrons with large values of  $k_{||}$  will be confined within the copper when the spins are aligned. They will undergo total internal reflection at the copper-cobalt interface.

The Cu majority Fermi surface is the same as the minority, but for Co the majority and minority Fermi surfaces are quite different. The Co minority Fermi surface (not shown) is very complicated because it lies in the d-bands. Our calculations show that for every value of  $k_{||}$  in Cu there is an allowed value of  $k_{\perp}$  on the minority Co Fermi surface. This means that total internal reflection does not occur at the Co-Cu interface for the minority electrons even though the difference in electronic structures is larger in this channel than in the majority channel.

Since the copper has a much lower resistance than the cobalt, the majority electrons that are confined to the copper layers will make a large contribution to the conductivity as can be seen in Figure 9. The contribution is lower when the cobalt moments are anti-parallel because the electrons with large values of  $k_{||}$  will only undergo total internal reflection on one side. The wave guide effect is most effective in increasing the GMR when the interfaces are smooth on an atomic scale, because it depends on the conservation of  $k_{||}$ .

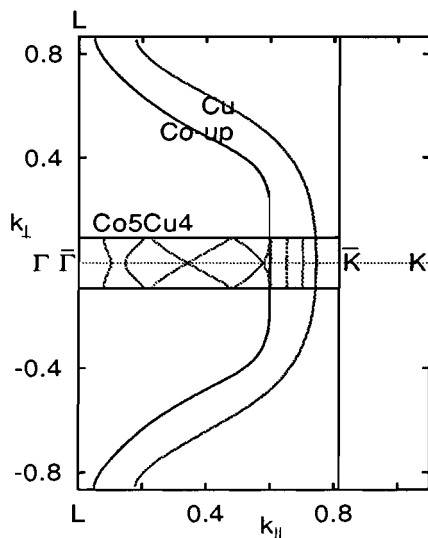


**Figure 9** Majority Fermi surfaces for Co, Cu, and Co5Cu4. For values of  $k_{||}$  greater than approximately 0.6 there are no allowed values of  $k_{\perp}$  in Co. An electron in a copper layer with a value of  $k_{||}$  greater than this value cannot scatter into the cobalt layers while conserving  $k_{||}$ . The Fermi surface of Co5Cu4 shows two modes that are localized on the copper layers.

## TECHNIQUE FOR CALCULATING ELECTRONIC STRUCTURE AND CONDUCTIVITY

In order to perform the calculation of the conductivity shown here we first performed a calculation of the electronic structure of the material using first-principles techniques. The problem of many electrons interacting with each other was treated in a mean field approximation using the Local Spin Density Approximation (LSDA) which has been shown to be quite accurate for determining electronic densities and interatomic distances and forces. It is also known to reliably describe the magnetic structure of transition metal systems.

The LSDA approach requires simultaneous self-consistent solutions of the Schrödinger and Poisson equations. This was accomplished using the Layer Korringa-Kohn-Rostoker technique<sup>6</sup> which has many useful features for calculations of properties of layered systems. It is, for example, one of only a few electronic structure techniques that can treat non-periodic infinite systems. It also has the virtue that the computational time required for a calculation scales linearly with the number of different layers, not as the third power as most other techniques.

After we obtained the self-consistent electronic structure of the magnetic multilayers we calculated the non-local conductivity by evaluating the quantum mechanical linear response of the current to the electric field using an approach developed by Kubo and Greenwood. In this approach the conductivity is obtained from a configurational average of two one-electron Green functions<sup>7</sup>,

$$\sigma_{\mu\nu}^{ij,s} = \frac{1}{4} \sum_{p,p'=\pm 1} (pp') \bar{\sigma}_{\mu\nu}^{ij,s}(\epsilon_F + i\eta p, \epsilon_F + i\eta p'),$$

$$\bar{\sigma}_{\mu\nu}^{ij,s}(z_1, z_2) = -\frac{\hbar}{2\pi^2 \Omega_i} \left\langle \int_{\Omega_i} dr \int_{\Omega_j} dr' j_\mu(r) G^s(r, r'; z_1) j_\nu(r') G^s(r', r, z_2) \right\rangle.$$

Here  $G^s(r, r'; z_1)$  is a Green function for electron propagation between points in cells  $i$  and  $j$ . The current operator is represented by  $j_\mu(r)$ , and the angular brackets indicate a configurational average. The layer dependent conductivity,  $\sigma_{\mu\nu}^{IJ,s}$ , is obtained by summing  $\sigma_{\mu\nu}^{ij,s}$  over sites  $i$  in layer  $I$  and sites  $j$  in layer  $J$ . In the calculations described here, the electron scattering processes were modeled by a phenomenological scattering rate which varied from layer to layer and which were envisioned as accounting for impurity, phonon, magnon, and other scattering processes. The vertex corrections corresponding to the scattering-in terms in the Boltzmann equation were not included because they depend on the details of the scattering process.

## CONCLUSIONS

The electronic structure, magnetic structure, and transport properties of magnetic multilayers can be calculated efficiently using first principles-based methods implemented within the layer KKR technique. Our calculations demonstrate the existence of two mechanisms which lead to GMR for the "current in the plane" geometry. One mechanism involves the non-local nature of conduction. In this mechanism GMR arises from electrons which are accelerated by the electric field in one ferromagnetic layer and travel through the spacer layer to the other ferromagnetic layer where they contribute to the current. This mechanism is optimized by minimizing spin-independent scattering and maximizing spin dependent scattering and the spin-dependence of total reflection and transmission at the interfaces. The second mechanism that can contribute to GMR is a wave guide effect in which electrons with certain values of momentum parallel to the interfaces undergo total internal reflection, confining the electrons to one of the layers. This effect can lead to a GMR if the electron is confined to a layer in which the mean free path is long. This mechanism is maximized by interfaces that are smooth on an atomic scale and by a very long mean free path in the layer in which the electrons are confined.

## ACKNOWLEDGMENTS

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# AB INITIO MOLECULAR DYNAMICS SIMULATIONS OF LIQUID ALLOYS: NETWORK FORMATION, STRUCTURE FACTORS AND ELECTRICAL CONDUCTIVITY OF NASN ALLOYS

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## INTRODUCTION

Many liquid alloys, in particular, the alkali-group IV alloys, exhibit (Zintl) anion clustering and show strong effects of compound formation. A typical example of such Zintl systems are sodium-tin alloys. In the solid NaSn crystal the Zintl anions  $\text{Sn}_4^{4-}$  appear [1]. An interesting question is the stability of these anions in the liquid. Furthermore, the electrical conductivity of these alloys shows a strong dependence on composition [2]: For the limiting (sodium-rich or tin-rich) cases a metallic (small) conductivity appears, but for the nearly equimolar compositions a semi-metallic behavior - with a considerably smaller conductivity - is observed.

For recent experimental considerations of the NaSn alloys see, for example, [3]. An overview concerning older theoretical and experimental work on these alloys is given in [4].

A successful tool to describe and interpret experimental findings of liquids is to perform *ab initio* molecular dynamics (MD) simulations for the particular systems. We performed such simulations for 5 different compositions of NaSn - ranging from 20% to 80% of sodium - applying the Car-Parrinello technique [5].

From the obtained trajectories the following structural and electronic properties were extracted: (i) structure factors, (ii) stability of Sn complexes, in particular, the Zintl anions, and (iii) the electrical conductivities - which yield answers to the questions mentioned in the first paragraph.

In a previous paper the Car-Parrinello (CP) technique was applied to the *equimolar* NaSn alloy [6]. In a further publication [7] we extended these investigations to a wide range of compositions ranging from 20% up to 80% of sodium and discussed the static structure factors and the behaviour of the Zintl anions ( $\text{Sn}_4^{4-}$ ) in the molten alloys.

Here, we will shortly summarize these results again. After this, we will focus on our recent results for the electrical conductivity. This quantity we calculated using the Kubo-Greenwood formula [8].

Similar alloys have been investigated theoretically more and more in the last years: LiSi [9], CsPb [10], MgBi [11]. Such previous investigations on the conductivity of alloys were based on simulation data for only one composition. We analyze, for the first time, by means of computer simulation, the strong variation of the conductivity with concentration - ranging from metallic to semimetallic behaviour.

To interpret the strong dependence of the conductivity from composition, we also evaluated the electronic density-of-states and analyzed its specific atomic contributions. For this discussion and for comparison we also calculated the electrical conductivities and the electronic density-of-states using a simplified density-functional (DFT)- based LCAO scheme [12].

We will start with the description of the method. After that the results are presented. Finally a summary and an outlook are given.

## METHOD

The Car-Parrinello simulations were performed using the MOTECC-90 computer code [13]. All considered systems consist of 64 atoms in a cubic unit cell with a length of 23.4 a.u. and periodic boundary conditions. The plane-wave cut-off was chosen to be 6 Ryd. The atomic cores were described by the pseudopotentials of Bachelet et al. [14].

The data for our analysis were collected from "production runs" of about 10000 steps, corresponding to a total simulation time of approximately 2 ps. The temperature for each simulation was chosen as that value for which experimental data are available. In general, the temperature lies about 50 K above the corresponding melting point. A detailed description of the computational features and the simulation procedure - including systems and temperatures - is given in [7].

The electrical (AC) conductivity for a single configuration of each system is obtained using the Kubo-Greenwood formula [8]:

$$\sigma(\omega) = \frac{2\pi e^2}{3m^2\omega\Omega} \sum_m \sum_n \sum_{\alpha}^{occ \ unocc} |\langle \psi_m | \hat{p}_{\alpha} | \psi_n \rangle|^2 \cdot \delta(\varepsilon_n - \varepsilon_m - \hbar\omega),$$

where  $m$  and  $e$  are the electronic mass and charge, respectively.  $\Omega$  is the MD cell volume and  $\hat{p}_{\alpha}$  is the  $\alpha$  component of the momentum operator.

The extrapolation  $\omega \rightarrow 0$  gives the DC conductivity. A detailed description of this extrapolation procedure will be given elsewhere [15].

To calculate the conductivity of the whole liquid, one has to average the obtained function  $\sigma(\omega)$  for the configurations of an MD trajectory, which corresponds to an ensemble average. The corresponding averaged density-of-states (DOS) was computed considering the same configurations as described above for each case.

**Table 1.** Resistivities of NaSn alloys with different compositions, in  $\mu\Omega\text{cm}$ .

| % Na | Exp. [2] | CP calc. | LCAO calc. |
|------|----------|----------|------------|
| 20   | 110±0.2  | 200± 50  | 230± 80    |
| 40   | 274±1    | 310±100  | 400±100    |
| 50   | 426±5    | 420±100  | 800±200    |
| 57   | 658±10   | 630±100  | 850±200    |
| 80   | 426±5    | 380±100  | 180±100    |

For comparison, we applied also a simplified LCAO-DFT method to get the conductivity by means of the Kubo-Greenwood formula. This method is a “hybrid” between *ab initio* and empirical methods and is described in detail in Ref. [12]. It allows a faster computation of the electronic properties and the consideration of larger supercells than the Car-Parrinello method. Within this scheme it is also possible to split the total DOS into fractions referring to the sodium and tin atoms, respectively, i.e. to get the partial densities-of-states.

**RESULTS AND DISCUSSION**

**Structure factors and stability of Zintl ions**

The obtained static structure factors agree well with the experimental ones [4], all trends of the peak positions are reproduced correctly. There are only small deviations from the experiments (i) due to the pseudopotential (slightly too small bond lengths which correspond to slightly too large peak positions in the reciprocal lattice) and (ii) correct positions but a wrong trend in the heights of the prepeaks. For a detailed description see Ref. [7].

An essential result of the simulations is that the Zintl anions  $\text{Sn}_4^{4-}$  for the equimolar case do not survive in the liquid. They form (dynamical) networks. For the liquid with 80% of sodium, the suggested “octet compounds”  $\text{SnNa}_4$  do not exist, and only isolated tin atoms or tin dimers appear.

**Electrical conductivity**

The resistivities  $\rho$  corresponding to the DC conductivities  $\sigma(0)$  calculated for each composition are given in Table 1, third column. For comparison, in the forth column also the results for  $\rho$  obtained with the LCAO-DFT scheme [12] are given. The CP as well as the LCAO results reproduce the measured strong dependence of  $\rho$  on the composition correctly. The CP results agree with the experiments very well. The only exception is the composition with 20% sodium where the relative deviation is about 100%; however, the absolute deviation is small.

This strong dependence of the conductivity on the composition can be understood qualitatively considering the densities-of-states. The DOS's from the LCAO calculation, splitted into their atomic contributions (partial DOS's), are given in Fig. 1 and can be discussed as follows:

The contributions to the DOS from sodium and tin are well separated in energy

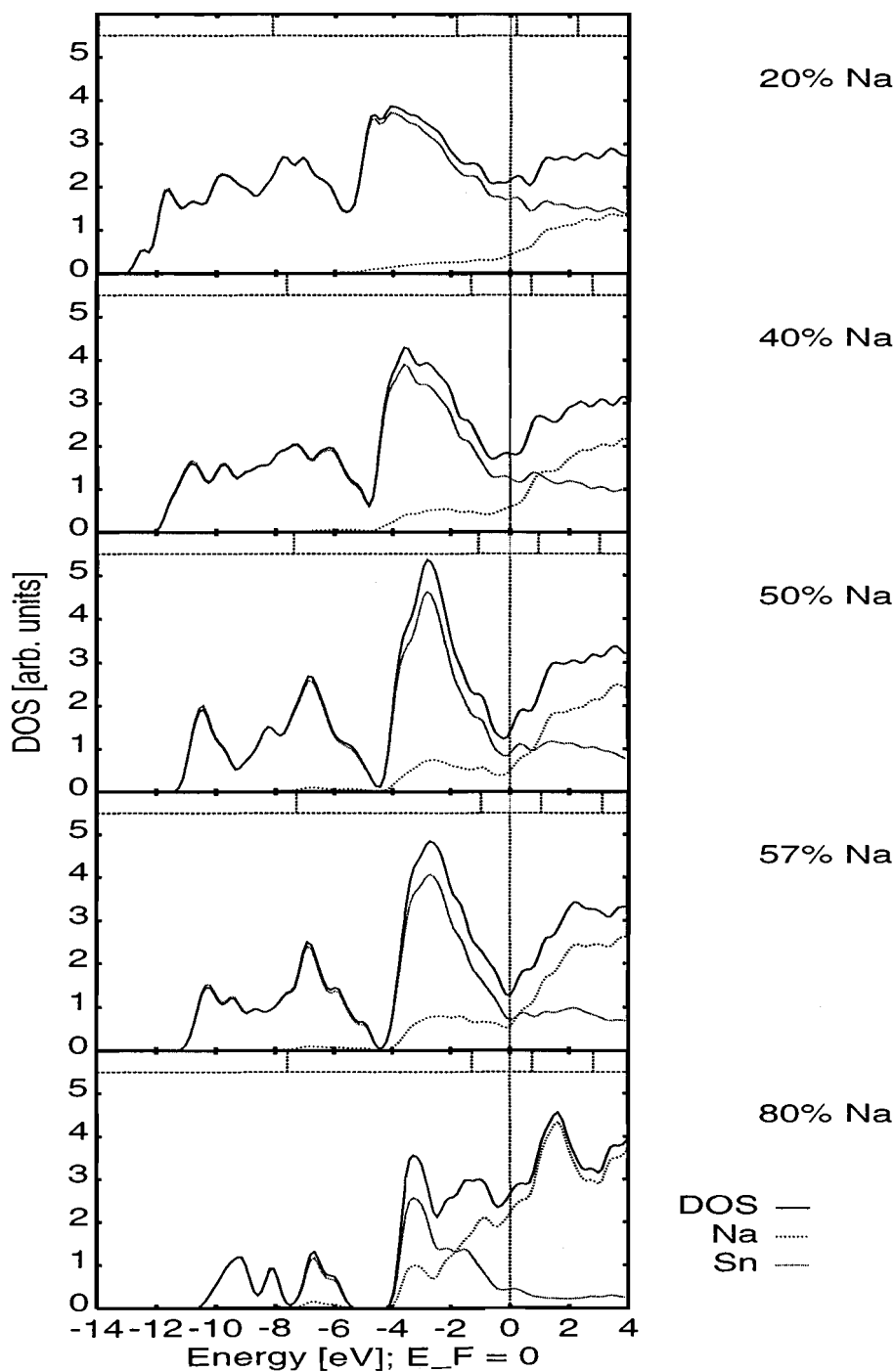


**Figure 1.** Densities-of-states and partial densities-of-states corresponding to Na and Sn for different compositions of liquid NaSn.



(due to the largely different atomic valence states of sodium and tin): The low-energy region is dominated by the *sp*-band of tin, whereas for high energies the *sp*-band of sodium becomes dominant.

For compositions with a small content of sodium the Fermi energy  $E_F$  lies in the *sp*-band of tin. This corresponds to a high DOS at  $E_F$  and therefore to a high (metallic) conductivity.

For compositions with 50 and 57% sodium  $E_F$  lies within the tail of the partial DOS of the *sp*-band of tin, but  $E_F$  has still not reached the region where the partial DOS of sodium is large. This yields a small DOS (pseudogap) for these cases at the Fermi level. Therefore, one gets an explanation for the minimum of the conductivity (i.e. the maximum of the resistivity) near the equimolar composition, as can be seen in Table 1. (Analogously, for solid equimolar  $\beta$ -NaSn even an indirect band gap at the Fermi level was reported in literature [16].)

In compositions with excess sodium the situation changes again: The Fermi level is now shifted up into the *sp*-band of sodium, yielding again a metallic behaviour like in the tin-rich cases.

## SUMMARY, OUTLOOK

We have performed *ab initio* MD simulations for 5 different compositions of liquid NaSn alloys. The calculated structure factors agree well with experimental data. The Zintl anions  $\text{Sn}_4^{4-}$  do not survive in the liquid and form networks. To investigate the problems with the prepeak arising from the finite supercell, MD simulations are in progress for larger supercells using the LCAO scheme [12]. The first results suggest that the essential conclusions given above are correct.

Furthermore, the electrical conductivities of liquid Na-Sn alloys for the five compositions are determined with the Kubo-Greenwood scheme, using the trajectories from our *ab initio* MD simulations. The calculated values reproduce the measured strong variation of the conductivity with the Na (or Sn) concentration very well. The small (semimetallic) conductivity of the alloys with nearly equimolar composition can be explained by the position of the Fermi energy between the occupied *sp*-band of tin and the *sp*-band of sodium.

The experiments [2] yielded also a considerable temperature dependence of the conductivities - including solid phases too [3]. Hence, we are going to consider now the  $T$  dependence of the conductivity for the liquid alloys.

In addition, for the sodium-antimony alloy, where the Zintl anions are Sb spiral chains, *ab initio* MD simulations are in progress.

## ACKNOWLEDGEMENT

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# INVESTIGATION OF GALVANO-MAGNETIC PROPERTIES OF TRANSITION METAL ALLOY SYSTEMS USING THE KUBO-GREENWOOD EQUATION

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## INTRODUCTION

The galvano-magnetic effects, i.e. the spontaneous magnetoresistance anisotropy (SMA) and the anomalous Hall resistivity (AHR) observed in spontaneously magnetized materials are used since decades in sensor technology [1]. Although it has been pointed out more than 40 years ago that these effects are caused by spin-orbit coupling, i.e. are of intrinsic origin and not due to an external magnetic field [2], a thorough theoretical description for them could be given only very recently by Banhart and Ebert [3]. Since then detailed theoretical investigations of the residual ( $T = 0$  K) resistivity properties of disordered  $\text{Fe}_x\text{Ni}_{1-x}$  [3],  $\text{Co}_x\text{Pd}_{1-x}$  and  $\text{Co}_x\text{Pt}_{1-x}$  [4] alloys have been performed. The theoretical approach of Banhart and Ebert is based on the Kubo-Greenwood-formalism with the underlying electronic structure described within the Dirac-formalism for magnetic solids. This ensures that the sources of galvano-magnetic effects – spin-orbit coupling and magnetization – are accounted for on the same level. As will be shown, additional insight into the mechanism giving rise to the SMA and AHR can be obtained by model calculations for which relativistic effects are manipulated. Furthermore it is demonstrated that performing scalar and fully relativistic calculations in parallel, it is possible to check the two-current model [2, 5, 6] that has been used so far to deal with the galvano-magnetic effects in magnetic solids.

## THEORETICAL FRAMEWORK

Application of the Coherent Potential Approximation (CPA) alloy theory in connec-

tion with the multiple scattering or Korringa-Kohn-Rostoker (KKR) method of band structure calculation allows for a very accurate determination of the single-particle Green function at the Fermi energy  $E_F$ ,  $G^+(E_F)$ , and that way also of the conductivity tensor  $\sigma$  via the Kubo-Greenwood equation [7]:

$$\sigma_{\mu\nu} = \frac{\hbar}{\pi V_{\text{cryst}}} \text{Tr} \left\langle j_\mu \text{Im} G^+(E_F) j_\nu \text{Im} G^+(E_F) \right\rangle_{\text{conf}}. \quad (1)$$

Here  $j_\mu$  is the  $\mu$ -th spatial component of the electronic current operator  $\mathbf{j}$  and  $\langle \dots \rangle_{\text{conf}}$  denotes the atomic configuration average for a disordered alloy.

Adopting the spin-polarized relativistic (SPR) version of the KKR-CPA method, the sources of the galvano-magnetic effects are properly included in the description of the underlying electronic structure. Furthermore, this approach accounts for the reduction in symmetry that is caused by the simultaneous occurrence of spin magnetism and spin-orbit coupling and is reflected by the form of the  $\sigma$  tensor. For example, for cubic systems with the magnetization along the z-axis,  $\sigma$  is – in contrast to the paramagnetic case – no more diagonal with identical elements, but has the form:

$$\rho = \sigma^{-1} = \begin{pmatrix} \rho_\perp & -\rho_H & 0 \\ \rho_H & \rho_\perp & 0 \\ 0 & 0 & \rho_\parallel \end{pmatrix}. \quad (2)$$

Here  $\rho_\parallel$  and  $\rho_\perp$  are the transverse and longitudinal resistivities with respect to the magnetization direction, respectively. The off-diagonal element  $\rho_H$  represents the spontaneous or anomalous Hall resistivity (AHR) [3]. Conventionally, the anisotropy of the resistivity is expressed by the SMA ratio

$$\frac{\Delta\rho}{\bar{\rho}} = \frac{\rho_\parallel - \rho_\perp}{\bar{\rho}} \quad (3)$$

where  $\bar{\rho} = \frac{1}{3}(2\rho_\perp + \rho_\parallel)$  is the isotropic resistivity.

Campbell et al. [5] proposed the very simple expression

$$\frac{\Delta\rho}{\bar{\rho}} = \gamma \left( \frac{\rho^\uparrow}{\rho^\downarrow} - 1 \right) \quad (4)$$

for the SMA ratio that has extensively been used in the past for the interpretation of experimental data. This expression relies on the two-current model that assumes the existence of partial resistivities  $\rho^{(\uparrow)}$  for both spin subsystems with  $1/\bar{\rho} = 1/\rho^\uparrow + 1/\rho^\downarrow$ . Furthermore, spin-orbit coupling is represented by the phenomenological parameter  $\gamma$ , that is meant to describe the coupling of both spin subsystems.

## RESULTS AND DISCUSSION

To investigate the connection between  $\Delta\rho/\bar{\rho}$  and  $\rho_H$  and the various relativistic effects two types of model calculations were performed: i) the speed of light  $c$  and that way all relativistic effects have been varied artificially, ii) the strength of the spin-orbit coupling has been manipulated separately [8].

Results for the SMA  $\Delta\rho$  of permalloy  $\text{Fe}_{0.2}\text{Ni}_{0.8}$  as a function of the scaling parameters  $(c_0/c)^2$  ( $c_0$  the proper speed of light) and  $\xi$ , scaling the spin-orbit coupling strength, are shown in Fig. 1. First of all one notes that the fully relativistic calculations with  $(c_0/c)^2 = 1$  or  $\xi = 1$ , are in very satisfying agreement with experiment.

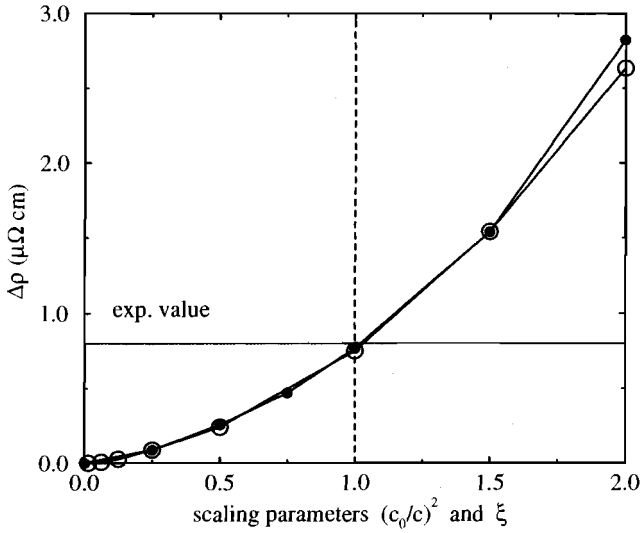


Figure 1: Spontaneous magnetoresistance anisotropy  $\Delta\rho$  of  $\text{Fe}_{0.2}\text{Ni}_{0.8}$  as a function of the scaling parameters  $(c_0/c)^2$  (○) and  $\xi$  (●). The experimental value is that from to Jaoul et al. [9].

As expected,  $\Delta\rho$  vanishes if the strength of the spin-orbit coupling is reduced to 0 by reducing  $(c_0/c)^2$  or  $\xi$ , respectively. Both sets of model calculations give nearly the same results indicating that the so-called scalar relativistic effects due to the mass-velocity and Darwin-term, are of minor importance for the absolute value of  $\Delta\rho$ .

Very similar results are found for the Hall resistivity  $\rho_H$  (not shown here). Again, the fully relativistic value is in rather good agreement with experiment. Varying the strength of the spin-orbit coupling,  $\rho_H$  varies nearly quadratically with  $(c_0/c)^2$  or  $\xi$ , respectively, in the range from 0 to 1. However, for higher values, i.e. in the super-relativistic region, both theoretical data sets deviate stronger than in the case of  $\Delta\rho$ . This means that scalar relativistic effects may have quite an appreciable influence on the absolute value of  $\rho_H$ .

As could be demonstrated by both types of model calculations spin-orbit coupling may also have a very strong impact on the isotropic resistivity  $\bar{\rho}$  of a magnetic solid. For example, for  $\text{Fe}_{0.2}\text{Ni}_{0.8}$  it was found that  $\bar{\rho}$  decreases by a factor of 3 when the spin-orbit coupling is suppressed. This finding is obviously not compatible with the simple two-current model. Because the influence of the spin-orbit coupling is the more pronounced the higher the spin-polarization at the Fermi energy is, the use of the two-current model can be justified only for systems with a rather low spin-polarization at the Fermi energy. While for  $\text{Fe}_x\text{Ni}_{1-x}$  this condition is far from being met, the use of the two-current model can be justified to some extent for the alloy systems  $\text{Co}_x\text{Pd}_{1-x}$  and  $\text{Co}_x\text{Pt}_{1-x}$  as it is demonstrated by Fig. 2.

For both alloy systems the theoretical results for  $\bar{\rho}$  obtained in a fully relativistic are found in very satisfying agreement with the corresponding experimental data. In addition to these calculations a second set of calculations has been done making use of the two-current model. This means the partial resistivities  $\rho^{l(t)}$  have been calculated by performing scalar relativistic calculations for every spin subsystem separately. As can be seen, the resulting total isotropic resistivity  $\bar{\rho}$  is reasonably close to the fully relativistic result. Furthermore, one notes that the relative deviation of both sets of theoretical data is more pronounced for  $\text{Co}_x\text{Pd}_{1-x}$  than for  $\text{Co}_x\text{Pt}_{1-x}$ . This has to be

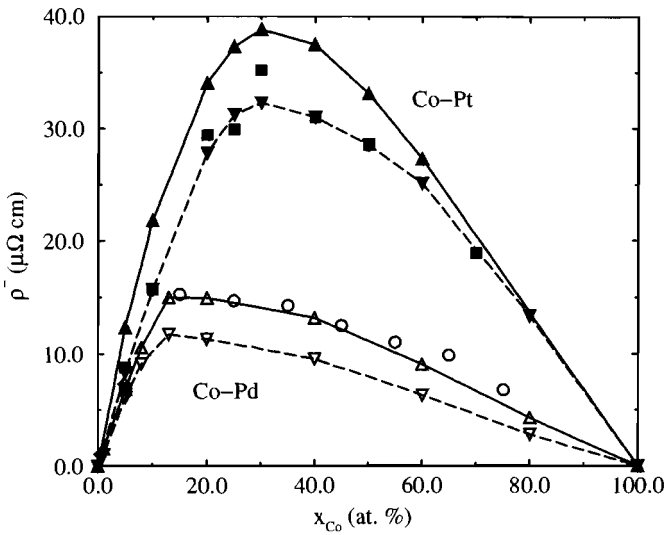


Figure 2: Residual isotropic resistivity  $\bar{\rho}$  of disordered  $\text{Co}_x\text{Pd}_{1-x}$  (open symbols) and  $\text{Co}_x\text{Pt}_{1-x}$  (full symbols) alloys. Theoretical results obtained in a fully relativistic way and using the two-current model are given by up and down-pointing triangles, respectively. All other symbols represent experimental data taken from various sources [13, 14, 15, 16].

expected because of the higher spin-polarization at the Fermi level for  $\text{Co}_x\text{Pd}_{1-x}$ .

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# BULK METALLIC GLASS FORMATION IN THE Pd-Ni-P and Pd-Cu-P ALLOY SYSTEMS

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## 1. INTRODUCTION

Since the first successful synthesis of glassy Au-Si and Pd-Si by P. Duwez and co-workers [1], the production of amorphous alloys has been associated with the rapid solidification of melts at cooling rates on the order of  $10^6$  K/sec. In these and many other alloys, high cooling rates are necessary to avoid the crystallization of the undercooled melt while it is quenched from the liquidus temperature  $T_l$  to the glass transition temperature,  $T_g$ . The required fast cooling rate restricts at least one of the dimensions of the amorphous products to less than about 50  $\mu\text{m}$ . Because amorphous metallic alloys have many potential technological applications, the recent discovery that certain alloy melts can be quenched into bulk amorphous states has received great attention.

Formation of a metallic glass by melt-quenching requires bypassing the crystallization of the melt within the temperature regime  $T_l$  to  $T_g$ . This, in turn, requires avoiding both the heterogeneous and homogeneous nucleation of crystalline embryos. Heterogeneous nucleation can be minimized by removing from the melt all foreign inclusions (e.g. oxides). When this is achieved, the major competition to glass formation comes from homogeneous nucleation. Turnbull [2,3] studied homogeneous nucleation in undercooled melts and showed that the most important single parameter describing the nucleation rate is the ratio of  $T_g$  to  $T_l$ , called the reduced glass transition temperature  $T_{rg}$ . The solid curves in Figure 1 show homogeneous nucleation rates for various values of  $T_{rg}$  calculated using the parameters listed in [4]. The nucleation rate is negligible for  $T \rightarrow T_l$  (because the thermodynamic force for crystallization approaches zero) and for  $T \rightarrow T_g$  (because the nucleation rate is kinetically suppressed by the increasing glass viscosity). If we associate a smaller nucleation rate (positive abscissa) with a larger time period during which the undercooled liquid can exist without crystallizing, the homogeneous nucleation

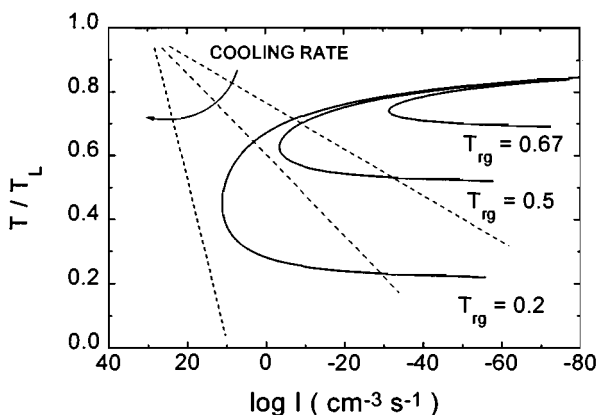


Figure 1. Calculated homogeneous nucleation rate for various values of  $T_{rg}$  as a function of temperature.

rate curves in the figure become equivalent to the customary T-T-T curves for crystallization. It is then clear that the larger the value of  $T_{rg}$ , the smaller the critical cooling rate required to avoid crossing the nose of the T-T-T curve, as indicated schematically by the three dashed lines.

For any given alloy system, the composition range for glass formation depends on its  $T_{rg}$  value (usually,  $T_g$  is weakly composition dependent) and on the imposed cooling rate. Because the liquidus temperature is lowest at and near eutectic compositions, glassy metallic alloys are easier to form by quenching melt of those compositions. The Pd-P and Ni-P binary systems have eutectics near the composition  $M_{80}P_{20}$  ( $M = Pd, Ni$ ). Both  $Pd_{80}P_{20}$  and  $Ni_{80}P_{20}$  can be prepared as thin amorphous ribbons at cooling rates  $> 10^4$  K/s. The ternary alloy  $Pd_{40}Ni_{40}P_{20}$  has  $T_{rg} = 0.65$  [3]. By quenching the melt in water, Chen produced bulk amorphous  $Pd_{40}Ni_{40}P_{20}$  alloy rods with diameters of 1-3 mm [5]. Using surface etching and thermal cycling to eliminate surface impurities, Drehman *et al.* [6] were able to produce amorphous  $Pd_{40}Ni_{40}P_{20}$  buttons with minor diameters of up to 5.3 mm; then, by fluxing molten  $Pd_{40}Ni_{40}P_{20}$  with dehydrated  $B_2O_3$ , Kui *et al.* [7] were able to further increase the minimum sample dimension to about 10 mm. These last two works demonstrate that in addition to a large  $T_{rg}$ , bulk glass formation requires the careful removal of heterogeneous nucleation centers. Several alloy compositions, listed in Table 1, have been found to be amenable to bulk glass formation with sample dimensions ranging from several mm to several cm. These sample dimensions could not have been achieved unless the critical cooling rates were on the order of 100 K/s, or lower. It is clear from the table that all these alloys have large values of  $T_{rg}$ . Most recently, Fe-based ferromagnetic bulk amorphous alloys have been synthesized [8,9] which may have important technological applications.

Although bulk amorphous  $Pd_{40}Ni_{40}P_{20}$  has been known for about 20 years, the bulk glass-forming range in the Pd-Ni-P system had not been investigated. It has been known, however, that using melt-spinning techniques (associated with cooling rates on the order of  $10^6$  K/s), amorphous  $Pd_{80-x}Ni_xP_{20}$  alloys can be produced over the whole metal composition range, i.e., from  $x = 0$  to  $x = 80$  [5]. Because a cm-size metallic sample cannot be cooled at a rate faster than about 100 K/s, the metal composition range



**Table 1.** Bulk glass forming alloy systems and the production methods. *d* is the smallest sample dimension.

| Alloy system                                      | Typical Composition                                                                            | $T_{rg}$ | Synthesis method | <i>d</i> (mm)  | Ref.      |
|---------------------------------------------------|------------------------------------------------------------------------------------------------|----------|------------------|----------------|-----------|
| Pd-Cu-Si                                          | Pd <sub>78</sub> Cu <sub>6</sub> Si <sub>16</sub>                                              | 0.63     | WQ               | 1-3            | [5]       |
| Pd-Ni-P, Pt-Ni-P                                  | Pt <sub>48</sub> Ni <sub>32</sub> P <sub>20</sub>                                              | ~ 0.60   | WQ               | 1-3            | [5]       |
| Pd <sub>40</sub> Ni <sub>40</sub> P <sub>20</sub> | Pd <sub>40</sub> Ni <sub>40</sub> P <sub>20</sub>                                              | 0.59     | FX               | 5-10           | [6,7]     |
| Pd-Ni-P                                           | Pd <sub>40</sub> Ni <sub>40</sub> P <sub>20</sub>                                              | 0.59     | FXWQ             | 10-25,<br>> 25 | [10]      |
| Pd-Cu-P                                           | Pd <sub>40</sub> Cu <sub>40</sub> P <sub>20</sub>                                              | 0.64     | FXWQ             | 7              | This work |
| Au-Pb-Sb                                          | Au <sub>55</sub> Pb <sub>22.5</sub> Sb <sub>22.5</sub>                                         | 0.63     | QLN              | 1.5            | [11]      |
| La-Al-Ni, La-Al-Cu                                | La <sub>55</sub> Al <sub>25</sub> Ni <sub>20</sub>                                             | 0.68     | DC               | 3              | [12]      |
| Zr-Al-Ni-Cu                                       | Zr <sub>65</sub> Al <sub>7.5</sub> Ni <sub>10</sub> Cu <sub>17.5</sub>                         | 0.58     | WQ               | 16             | [13]      |
| Mg-Cu-Y, Mg-Ni-Y                                  | Mg <sub>65</sub> Cu <sub>25</sub> Y <sub>10</sub>                                              | 0.60     | MC               | 4              | [14,15]   |
| Zr-Ti-Cu-Ni-Be                                    | Zr <sub>41.2</sub> Ti <sub>13.8</sub> Cu <sub>12.5</sub> Ni <sub>10</sub> Be <sub>22.5</sub>   | 0.67     | MC               | > 14           | [16,17]   |
| Ti-Zr-Cu-Ni                                       | Ti <sub>34</sub> Zr <sub>11</sub> Cu <sub>47</sub> Ni <sub>8</sub>                             | 0.59     | MC               | 4              | [18]      |
| Fe-based alloys                                   | Fe <sub>73</sub> Al <sub>5</sub> Ga <sub>2</sub> P <sub>11</sub> C <sub>5</sub> B <sub>4</sub> |          | MC               | 1-2            | [8]       |
| Pd-Cu-Ni-P                                        | Pd <sub>40</sub> Cu <sub>30</sub> Ni <sub>10</sub> P <sub>20</sub>                             | 0.71     | WQ               | 40             | [19]      |
| Nd-Fe-Al                                          | Nd <sub>70</sub> Fe <sub>20</sub> Al <sub>10</sub>                                             | *        | MC, SC           | 4-12           | [20,21]   |

DC = die casting; FX = fluxing; MC = mold casting; WQ = water quenching;  
FXWQ = fluxing followed by water quenching; SC = suction casting;  
QLN = quenching into liquid nitrogen.      \* No glass transition observed.

for *bulk* glass formation in the Pd-Ni-P system is narrower. Using an improved fluxing technique, we have recently studied bulk glass formation in the Pd-Ni-P system, and found that bulk amorphous alloy rods with diameters of 10 mm can be synthesized over a wide composition range [10,22]. We have also found, for the first time, that bulk amorphous rods with diameters up to 7 mm can be produced in the Pd-Cu-P and Pd-Ni-Fe-P systems [23]. Compared to the other bulk glass systems listed in Table 1, the Pd-Ni-P and Pd-Cu-P systems have the advantage of having only three elements, and being relatively easy to prepare. In this paper, we report the composition ranges for bulk glass formation in the Pd-Ni-P and Pd-Cu-P systems and the thermal and elastic properties of these bulk amorphous alloys.

## 2. EXPERIMENTAL

The bulk amorphous alloys were prepared by two synthesis methods. To prepare the Pd-Ni-P alloys, commercial  $\text{Ni}_2\text{P}$  powder (99.5% pure) was arc melted under a purified argon atmosphere to produce  $\text{Ni}_2\text{P}$  ingots. Then, solid  $\text{Ni}_2\text{P}$ , palladium (99.99% pure), and nickel (99.99% pure) were arc-melted to form alloy ingots of the desired composition. These alloys were placed in fused silica tubes, and repeatedly purified in molten  $\text{B}_2\text{O}_3$ , as described in Refs. [6,7]. Finally, the fused silica tubes containing the melt and the flux were quenched in water.

To synthesize bulk amorphous Pd-Cu-P alloys, we started by ball-milling elemental powders of Pd (99.95% pure), Cu (99% pure), and P (99.99% pure) in a SPEX 8000 laboratory ball mill for about 10 hours. The ball-milling was carried out inside an argon-filled glove box containing less than 0.1 ppm oxygen. The ball-milled powder was then placed in a fused silica tube together with dehydrated  $\text{B}_2\text{O}_3$  and processed as described above. The quenched Pd-Ni-P and Pd-Cu-P rods were sectioned with a low-speed diamond saw to prepare samples for x-ray diffraction, differential scanning calorimetry, and elastic moduli measurements.

## 3. BULK GLASS FORMATION RANGE

### (a) Pd-Ni-P

Using the  $\text{B}_2\text{O}_3$  fluxing technique, amorphous Pd-Ni-P alloy rods with a critical diameter of 10 mm can be formed over a wide composition range. The phosphorus content is restricted to around  $(20 \pm 5)$  at.%, whereas the palladium concentration can vary from 25 to 60 at.%, as illustrated in Figure 2. Among these alloys,  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  has the highest glass forming ability, and a 300-gram bulk amorphous cylinder, 25 mm in diameter and 50 mm in length, can be easily synthesized [10]. The cross section of this cylinder was examined by x-ray diffraction and it showed that the whole sample was amorphous. Clearly, this size is by no means the upper limit for bulk glass formation in  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ .

### (b) Pd-Cu-P

As shown in Fig. 3, bulk Pd-Cu-P glasses also require about 20 at.% P. The palladium concentration needed to form bulk amorphous rods with diameters of 7 mm is restricted to 40 - 60 at.%, which is narrower than that for Pd-Ni-P glasses. During these tests, we noticed that upon replacing part of the Cu by Ni, the glass forming ability of the

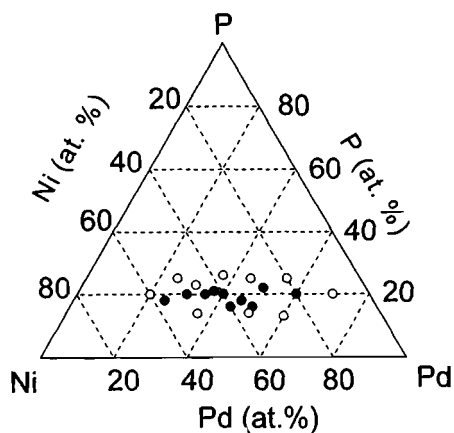


Figure 2. Bulk glass formation range in Pd-Ni-P system. Filled circles denote the formation of amorphous phase, open circles denote the formation of crystalline phases.

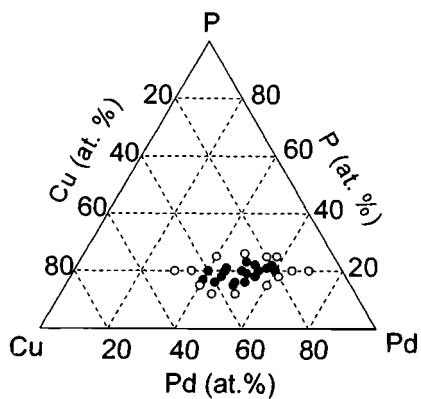


Figure 3. Bulk glass formation range in Pd-Cu-P alloys. Filled symbols are the compositions where amorphous rods with diameter of 7 mm can be formed, open circles represent the formation of crystalline phases.

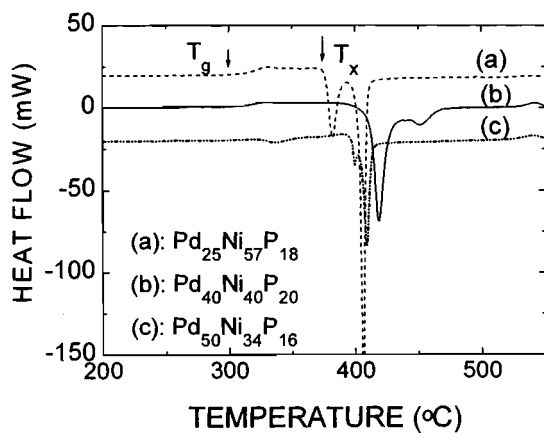


Figure 4. DSC traces for three bulk glassy Pd-Ni-P alloys at the heating rate of 20 K/min.

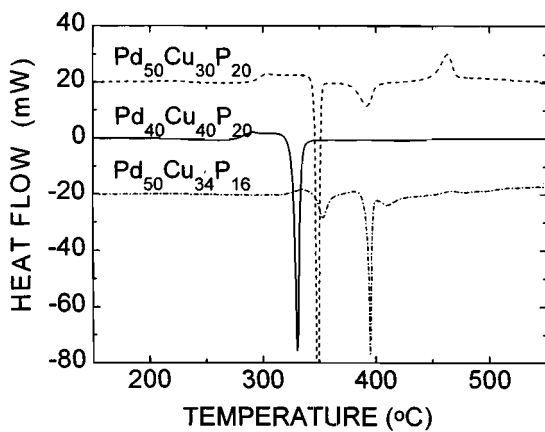


Figure 5. DSC traces for three bulk glassy Pd-Cu-P alloys at a heating rate of 20 K/min.

Pd-Cu-P alloys can be enhanced drastically. For example, amorphous  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  cylinders with a diameter of 16 mm can be readily obtained by fluxing followed by air-cooling (*i.e.* without quenching the molten alloy in water), while water quenching enables the formation of amorphous  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  cylinder of 40 mm in diameter [19]. The glass formability in the Pd-Ni-Cu-P system is under investigation.

#### 4. GLASS TRANSITION AND CRYSTALLIZATION

The values of  $T_g$  and  $T_x$  are of technological importance. For most metallic glasses,  $T_x$  is close or even lower than  $T_g$ . Bulk glasses, however, are characterized by a large value of  $\Delta T$ . This may be due to the fact that bulk glasses are usually formed at or near the compositions of deep eutectics. Thus, in the absence of metastable crystalline phases at the eutectic composition, crystallization would require extensive solute partitioning and long-range diffusion. In practice, a large value of  $\Delta T$  is important because within the temperature range  $T_x - T_g$ , the amorphous alloy can be used to produce near-net shape components using techniques such as injection-molding. Figures 4 and 5 are the DSC traces of a number of selected bulk amorphous Pd-Ni-P and Pd-Cu-P alloys obtained at a scanning rate of 20 K/min. The values of  $T_g$ ,  $T_x$ ,  $\Delta T$ , and  $\Delta H_x$  are listed in Table 2.

From Table 2, it is clear that the variations of the glass transition temperature as a function of the composition for amorphous Pd-Ni-P alloys is small. The weak composition dependence of  $T_g$  in Pd-Ni-P alloys is consistent with previously reported results [24,25], where  $T_g$  of glassy  $\text{Pd}_{80-x}\text{Ni}_x\text{P}_{20}$  alloys were found to be between 585 and 602 K when  $x$  varies from 0.15 to 0.8. In contrast,  $T_g$  for bulk amorphous  $\text{Pd}_x\text{Cu}_{80-x}\text{P}_{20}$  alloys increases gradually as the palladium concentration increases, as illustrated in Figure 6.

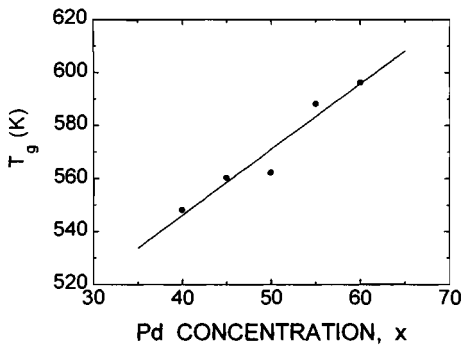


Figure 6. Composition dependence of the glass-transition temperature  $T_g$  for bulk amorphous  $\text{Pd}_x\text{Cu}_{80-x}\text{P}_{20}$ .

**Table 2:** Values of  $T_g$ ,  $T_x$ ,  $\Delta T$  and the crystallization enthalpy,  $\Delta H_x$ , for bulk amorphous Pd-Ni-P and Pd-Cu-P alloys determined by DSC at a scanning rate of 20 K/min.

| Composition                                       | $T_g$ (°C) | $T_x$ (°C) | $\Delta T$ (K) | $\Delta H_x$ (kJ/mole) |
|---------------------------------------------------|------------|------------|----------------|------------------------|
| Pd <sub>25</sub> Ni <sub>57</sub> P <sub>18</sub> | 285        | 377        | 92             | 5.71                   |
| Pd <sub>30</sub> Ni <sub>50</sub> P <sub>20</sub> | 310        | 400        | 90             | 5.94                   |
| Pd <sub>35</sub> Ni <sub>45</sub> P <sub>20</sub> | 308        | 410        | 102            | 5.94                   |
| Pd <sub>37</sub> Ni <sub>42</sub> P <sub>21</sub> | 310        | 405        | 95             | 5.36                   |
| Pd <sub>40</sub> Ni <sub>40</sub> P <sub>20</sub> | 303        | 405        | 102            | 7.37                   |
| Pd <sub>44</sub> Ni <sub>40</sub> P <sub>16</sub> | 300        | 395        | 95             | 6.10                   |
| Pd <sub>46</sub> Ni <sub>36</sub> P <sub>18</sub> | 300        | 389        | 89             | 6.20                   |
| Pd <sub>50</sub> Ni <sub>34</sub> P <sub>16</sub> | 292        | 396        | 104            | 4.76                   |
| Pd <sub>50</sub> Ni <sub>28</sub> P <sub>22</sub> | 311        | 403        | 92             | 6.06                   |
| Pd <sub>60</sub> Ni <sub>20</sub> P <sub>20</sub> | 315        | 371        | 56             | 3.37                   |
| Pd <sub>40</sub> Cu <sub>40</sub> P <sub>20</sub> | 275        | 326        | 51             | 2.66                   |
| Pd <sub>40</sub> Cu <sub>43</sub> P <sub>17</sub> | 281        | 324        | 43             | 3.18                   |
| Pd <sub>44</sub> Cu <sub>40</sub> P <sub>16</sub> | 300        | 331        | 31             | 3.59                   |
| Pd <sub>45</sub> Cu <sub>35</sub> P <sub>20</sub> | 287        | 360        | 73             | 3.52                   |
| Pd <sub>50</sub> Cu <sub>30</sub> P <sub>20</sub> | 289        | 346        | 57             | 3.92                   |
| Pd <sub>50</sub> Cu <sub>34</sub> P <sub>16</sub> | 316        | 344        | 28             | 4.41                   |
| Pd <sub>50</sub> Cu <sub>35</sub> P <sub>15</sub> | 312        | 340        | 28             | 4.04                   |
| Pd <sub>50</sub> Cu <sub>27</sub> P <sub>23</sub> | 292        | 319        | 27             | 3.83                   |
| Pd <sub>55</sub> Cu <sub>25</sub> P <sub>20</sub> | 315        | 382        | 67             | 3.75                   |
| Pd <sub>58</sub> Cu <sub>20</sub> P <sub>22</sub> | 323        | 372        | 49             | 2.91                   |
| Pd <sub>60</sub> Cu <sub>20</sub> P <sub>20</sub> | 323        | 387        | 64             | 4.04                   |

The crystallization of glassy Pd-Ni-P and Pd-Cu-P alloys is complicated by the formation of metastable crystalline phases [26]. The final (stable) crystallization product consists of a mixture of a (Pd,Ni) or (Pd,Cu) fcc solid solution and more than one kind of metal phosphide of low crystallographic symmetry. Donovan *et al.* [27] used transmission electron microscopy (TEM) and X-ray microanalysis to study the microstructure of slowly cooled crystalline Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub>. They identified the compositions of the metal phosphides to be Pd<sub>34</sub>Ni<sub>45</sub>P<sub>21</sub> and Pd<sub>68</sub>Ni<sub>14</sub>P<sub>18</sub>.

## 5. ELASTIC PROPERTIES

The elastic properties of bulk amorphous Pd<sub>25</sub>Ni<sub>57</sub>P<sub>18</sub>, Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub>, Pd<sub>50</sub>Ni<sub>34</sub>P<sub>16</sub>, Pd<sub>40</sub>Cu<sub>40</sub>P<sub>20</sub>, Pd<sub>50</sub>Cu<sub>30</sub>P<sub>20</sub>, and Pd<sub>60</sub>Cu<sub>20</sub>P<sub>20</sub> alloys were measured by resonant ultrasound spectroscopy (RUS). In this technique, the spectrum of mechanical resonances for a parallelepiped sample is measured and compared with a theoretical spectrum calculated for a given set of elastic constants. The true set of elastic constants is calculated by a recursive regression method that matches the two spectra [28,29].

An isotropic and non-magnetic amorphous alloy has only two independent second order elastic constants. The other elastic moduli are related through the equations [30]:

$$C_{12} = C_{11} - 2 C_{44}, \quad (1)$$

$$E = \frac{(C_{11} - C_{12})(C_{11} + 2C_{12})}{(C_{11} + C_{12})}, \quad (2)$$

$$B = \frac{1}{3}(C_{11} + 2C_{12}), \quad (3)$$

$$\nu = \frac{C_{12}}{C_{11} + C_{12}}, \quad (4)$$

where  $E$ ,  $B$ , and  $\nu$  are the Young's modulus, the bulk modulus, and the Poisson's ratio, respectively. The shear modulus  $G$  is simply  $C_{44}$ . Table 3 lists the elastic constants of a number of bulk amorphous Pd-Ni-P and Pd-Cu-P alloys. The typical experimental uncertainties of the RUS measurements are 0.8% for  $C_{11}$  and 0.05% for  $C_{44}$ .

Table 3 also lists the density  $\rho$  of these alloys, which was measured by the Archimedes' principle using pure ethanol as immersion fluid. To monitor the accuracy of the measurements, the density of 99.999% pure Al shots was also measured and it was found to be within 0.4% from its accepted value.

The Debye temperature of the bulk amorphous alloys was calculated from the relation:

$$\Theta_D = \frac{h}{k_B} \left( \frac{9\rho N}{4\pi M} \right)^{1/3} \left( \frac{1}{V_L^3} + \frac{2}{V_T^3} \right)^{-1/3}, \quad (5)$$

where  $h$ ,  $k_B$ , and  $N$  are the Planck constant, the Boltzmann constant, and the Avogadro number, respectively;  $M$  is the mean atomic weight and  $\rho$  is the density. The longitudinal

**Table 3:** Room-temperature elastic constants, density, and the Debye temperature  $\Theta_D$  of a number of Pd-Ni-P and Pd-Cu-P bulk amorphous alloys. The elastic moduli are in units of GPa and the density  $\rho$  is in units of  $\text{g/cm}^3$ .

| Sample                                                   | $C_{11}$ | $C_{12}$ | $C_{44}$ | $E$ | $B$ | $\nu$ | $\rho$ | $\Theta_D$ (K) |
|----------------------------------------------------------|----------|----------|----------|-----|-----|-------|--------|----------------|
| $\text{Pd}_{25}\text{Ni}_{57}\text{P}_{18}$              | 232      | 152      | 40.0     | 112 | 179 | 0.396 | 8.97   | 311            |
| $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$              | 229      | 156      | 36.6     | 103 | 180 | 0.405 | 9.36   | 286            |
| <sup>a</sup> $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ | 236      | 159      | 38.6     | 108 | 185 | 0.403 | 9.41   | 301            |
| $\text{Pd}_{50}\text{Ni}_{34}\text{P}_{16}$              | 230      | 152      | 39.2     | 110 | 178 | 0.397 | 9.84   | 285            |
| $\text{Pd}_{40}\text{Cu}_{40}\text{P}_{20}$              | 202      | 136      | 33.2     | 93  | 158 | 0.402 | 9.30   | 269            |
| $\text{Pd}_{50}\text{Cu}_{30}\text{P}_{20}$              | 205      | 139      | 32.7     | 92  | 161 | 0.405 | 9.46   | 262            |
| $\text{Pd}_{60}\text{Cu}_{20}\text{P}_{20}$              | 210      | 145      | 32.3     | 91  | 167 | 0.409 | 9.78   | 254            |

<sup>a</sup> Data from ref. [31]; the elastic constants were measured by the pulse-echo technique;  $\Theta_D$  was determined from low-temperature specific heat data.

and the transverse ultrasound velocities  $V_L$  and  $V_T$  are given by

$$V_L = \sqrt{\frac{C_{11}}{\rho}}, \text{ and } V_T = \sqrt{\frac{C_{44}}{\rho}}. \quad (6)$$

The calculated Debye temperatures are also listed in Table 3. From this table, it is clear that the elastic properties of the bulk amorphous Pd-Ni-P and Pd-Cu-P alloys change little with changing composition. The elastic moduli of the Pd-Cu-P alloys are slightly lower than those for the Pd-Ni-P alloys.

## 6. DISCUSSION

DTA curves for the melting of  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  and  $\text{Pd}_{40}\text{Cu}_{40}\text{P}_{20}$  alloys are shown in Figure 7. Our DTA curve for  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  is in agreement with previous results [32]. From this data, we calculate for these two alloys  $T_{rg}$  values as the ratio of  $T_g/T_l$  of 0.59 and 0.65, respectively. Notice that the melting of  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  occurs over a temperature interval of about 100 K, starting at  $T_m$  and ending at  $T_l$ . If one defines  $T_{rg}$  as the ratio  $T_g/T_m$ , then the  $T_{rg}$  value for  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  would be much higher, around 0.65, which is the value often quoted in the literature. The definition  $T_{rg} = T_g/T_l$  is more appropriate.

Using the fluxing technique, Lau and Kui [33] determined that the critical cooling rate for forming a 7-mm diameter bulk amorphous  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  cylinder was  $\sim 0.75$  K/sec. From this value, they estimated that the steady-state nucleation frequency was on the order of  $10^4 \text{ m}^{-3} \text{ s}^{-1}$ . On the other hand, Drehman and Greer [34] estimated that the steady state nucleation frequency at 590 K is  $\sim 10^6 \text{ m}^{-3} \text{ s}^{-1}$ , which is also the maximum



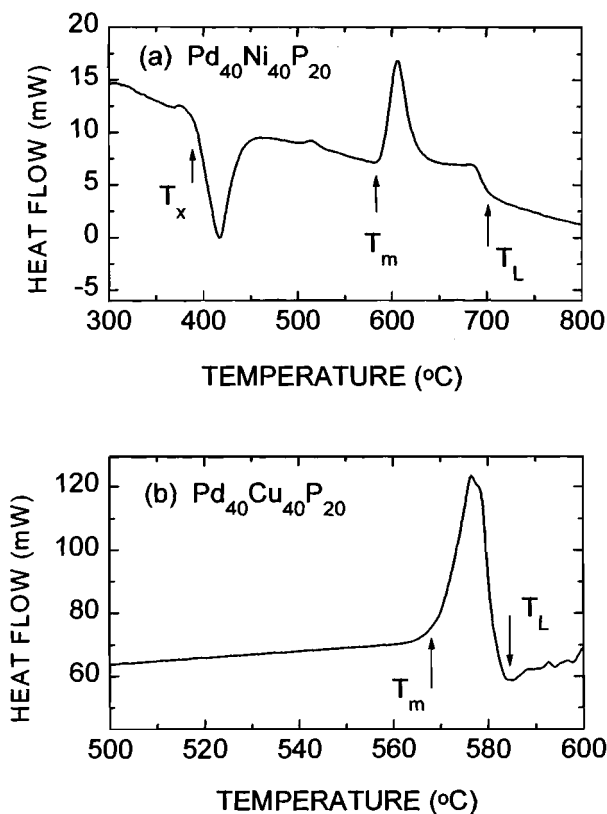


Figure 7. (a) DTA trace revealing the crystallization and melting of glassy  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ . (b) DSC trace of  $\text{Pd}_{40}\text{Cu}_{40}\text{P}_{20}$  alloy near its melting point.  $T_m$  is the beginning of the melting, while  $T_L$  indicates the liquidus temperature where melting completes. The scanning rate used for DTA and DSC measurements is 20 K/min.

nucleation frequency. These two values are the smallest ever found in a metallic system. From the measured nucleation frequency and an estimated crystal growth rate of  $\sim 10^{-10}$  m/s at 590 K, follows that the *theoretical* critical cooling rate for glass formation in  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  is  $10^{-3}$  K/s. There have been various attempts to measure the critical cooling rate in  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ . Willnecker *et al.* [35] reported an upper bound of 0.17 K/s. Using the fluxing technique, we found that mm-size  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  liquid can be vitrified without crystallization at a cooling rate of 0.34 K/s [23]. For such a low critical cooling rates, the thermodynamic properties of the undercooled  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  liquid can be measured for the first time over the entire undercooling regime, from the melting temperature down to the glass transition temperature [32]. In comparison, the critical cooling rate for glass formation in the multi-component  $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$  alloy is  $\sim 1$  K/s [17]. Thus the reported values of critical cooling rates for  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  are about 6 times lower than those of the beryllium containing bulk amorphous alloys. Our work to date suggests that the critical cooling rates in the quaternary Pd-Cu-Ni-P alloys are even smaller than those reported for the ternary Pd-Ni-P alloys.

## 7. CONCLUSIONS

Bulk metallic glasses were prepared in the Pd-Ni-P and Pd-Cu-P systems using a fluxing technique. The formation of bulk amorphous Pd-Cu-P alloys was reported here for the first time. For both alloy systems, bulk glass formation requires maintaining the phosphorus content near 20 at.%. In the Pd-Ni-P system, 10-mm diameter amorphous  $\text{Pd}_x\text{Ni}_{80-x}\text{P}_{20}$  rods can be formed for  $25 \leq x \leq 60$ . In the Pd-Cu-P system, 7-mm diameter amorphous  $\text{Pd}_x\text{Cu}_{80-x}\text{P}_{20}$  rods can be produced for  $40 \leq x \leq 60$ .

From all the ternary alloys studied,  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  has the highest glass formability, and 25-mm diameter amorphous cylinders, 50 mm in length, can be easily fabricated.

The glass stability of the Pd-Ni-P system is wider than that of the Pd-Cu-P system. For most bulk Pd-Ni-P glasses (10-mm diameter),  $\Delta T > 90$  K. The  $\Delta T$  values of bulk amorphous Pd-Cu-P alloys are considerably smaller, ranging from 27 to 73 K.

The elastic constants of bulk amorphous Pd-Ni-P and Pd-Cu-P alloys were determined using a resonant ultrasound spectroscopy technique. The Pd-Ni-P glasses are slightly stiffer than the Pd-Cu-P glasses. Within each alloy system, the Young's modulus and the bulk modulus show little change with alloy composition.

Of all the bulk glass forming systems so far investigated (Table 1), the ternary Pd-Ni-P system has the best glass formability. This alloy was one of the first bulk glasses discovered, yet it still remains the best in terms of glass formability. Upon replacing part of Ni by Cu, the critical cooling rates are expected to be further reduced.

## 8. ACKNOWLEDGMENTS

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# ELECTRONIC TOPOLOGICAL TRANSITIONS AND COMPOSITIONAL ORDER IN CuPd AND CuPt ALLOYS

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## INTRODUCTION

Varying the electron per atom ratio in random noble-transition metal alloys not only changes their Fermi volumes but also causes transitions in their Fermi Surface (FS) topologies (Electronic Topological Transitions or ETT<sup>1</sup>). As it is well known<sup>1</sup> the ETT's influence transport properties, elastic properties and electron-phonon interaction<sup>2</sup>. Moreover, as we have recently shown, they affect the crystal equilibrium volumes<sup>3</sup>. In this communication, we present a first principle comparative study, based on the relativistic Korringa Kohn Rostoker Coherent Potential Approximation (KKR-CPA)<sup>4</sup>, of CuPt and CuPd random alloys. These systems have a peculiar interest since, although isoelectronic, their phase diagrams are profoundly different<sup>5</sup>. In this paper, we attempt to trace the seeds of the low temperature phase equilibria of these alloys in the FS's of their homogeneous solid solution phases. In our analysis both the ETT theory and the Krivoglaz-Clapp-Moss<sup>6</sup> model (KCM) will prove useful.

At high temperature, CuPd and CuPt present a fcc solid solution phase in the whole range of Copper concentrations,  $c$ . Just below the equiatomic composition, in the range  $0.30 < c < 0.50$ , CuPd orders along the (001) direction into the "body centred" B2 structure (implying also a martensitic transition). On the other hand, in the broader range  $0.30 < c < 0.90$ , CuPt orders in a different fcc based structure, the  $L1_1$ , consisting in alternating Cu and Pt planes along (111). Furthermore, in the Cu rich region, both systems present similar behaviours. A cubic  $L1_2$  phase is observed about  $c=0.85$ , while about the ideal concentration,  $c=0.75$ , only long period superstructures (LPS) compatible with  $L1_2$  ordering are found. Interestingly, these alloys do not have a "symmetric" phase diagram, e.g.  $L1_2$  ordering is not observed about  $c=0.25$ .

As it is well known<sup>7-9</sup>, the FS affects the occurrence of LPS through the incommensurate concentration wave mechanism. This very frequently occurs when the random alloy FS's present large flat portions, whose connecting vector,  $\vec{q} = 2\vec{k}_F$ , is not commensurate with the lattice spacing. According to the Gyorffy and Stocks' concentration functional theory<sup>8,9</sup> and its recent generalisations<sup>10</sup>, the concentration waves susceptibility peaks at  $\vec{q}$ , indicating an instability of the homogeneous solid solution phase with respect to concentration fluctuations having the same wavevector. This mechanism, usually referred to as nesting, is the basis of the KCM model. On lowering the temperature, it could eventually drive the ordering transition. A classical example here is given by CuPd alloys<sup>9</sup> in the region about  $c=0.75$ . The ordering process here consists in alternating Cu and equiatomic Cu and Pd centred square planes, perpendicular to the (0,0,1) direction. For future reference, we observe that, whenever  $q$  is almost commensurate with the lattice interplanar distance, the ordering transition is favoured, while, if it is sensibly different, the occurrence of either ordering or even LPS is unlike, being frustrated by the lattice geometry. We also notice that the B2 phase, observed about the equiatomic region in CuPd, is, again, an ordering along (0,0,1).

Clark et al.<sup>11</sup> recently discovered another FS related mechanism in CuPt, different from the above mentioned nesting. In this case, the relevant contribution to the concentration waves susceptibility is due to the contemporary presence of the noble metal-like neck at the L point and the d hole pocket at X. The connecting vector of these Van Hove singularities belongs to the star  $\{1,1,1\}$  and is commensurate with the  $L1_1$  ordering. In fact, it produces a phase characterised by alternate hexagonal Cu and Pt planes, in the direction perpendicular to  $(1,1,1)$ .

We observe that, on increasing  $c$ , CuPt and CuPd FS's must change from the fcc transition metal like (say, octahedron centred at  $\Gamma$ , hole pockets at X connected at L by the jungle-gym structure) to the noble metal like (say, octahedron centred at  $\Gamma$ , neck at L) topology. Thus, similarities in their FS's are expected for. This suggests, in a naïve rigid band picture, that analogous ordering processes should occur in these isoelectronic systems, or, at least, that both the equiatomic CuPt and CuPd should show ordering tendencies along both the  $(0,0,1)$  and  $(111)$  directions. As a matter of fact, their experimental phase diagrams are different. As we shall see in the following, the relevant ETT's in CuPd and CuPt do not occur in the same order on varying  $c$ . Namely, we find that CuPd, opposite to CuPt, exhibits a simple metal like FS in a narrow concentration interval just above  $c=0.50$ . This could in firm the rigid band argument. At this point, two different scenarios are possible: i) the rigid band picture is essentially correct and a competition between the  $(0,0,1)$  and  $(1,1,1)$  orderings takes place, leading to different phases for the two alloys; ii) one of the two tendencies does not exist at all, at least for one of the above alloys.

We like to conclude this introduction observing, after Lifshitz, that a free energy excess is involved in each ETT. Thus, it might happen that, in order to avoid the energy cost involved in opening, say, a neck in the FS, the system might prefer to change its phase<sup>3</sup>. This could be the case of the martensitic transition observed in CuPd.

## CuPd AND CuPt FERMI SURFACES AND ORDERING TENDENCIES

We have calculated the Bloch Spectral Function<sup>12</sup> (BSF) at the Fermi energy,  $A_B(\vec{k}, \epsilon_F)$ , for fcc  $\text{Cu}_{0.20}\text{Pd}_{0.80}$  and  $\text{Cu}_{0.20}\text{Pt}_{0.80}$ , random alloys for various value of  $c$ . The site potentials used have been obtained ab initio via the relativistic LDA-KKR-CPA<sup>4</sup> method at the lattice parameters corresponding to the total energy minimum.

From the plots (Fig. 1) of the above BSF's along high symmetry lines it is possible to determine the relevant features of the corresponding FS's and the ETT's encountered on increasing  $c$ .  $\text{Cu}_{0.20}\text{Pd}_{0.80}$  FS is still very similar to that of pure Pd. The main features here are: i) Among the three peaks visible along the  $\Delta$  line, the first, on going from  $\Gamma$  to X, measures the electron octahedron centred at the  $\Gamma$  point. The remaining two peaks correspond to hole structures centred at X: that closest to X corresponds to a hole ellipsoid, the other broader peak belongs to an open structure, the so called jungle-gym, that, on increasing  $c$ , eventually disconnects at the L point.  $\text{Cu}_{0.20}\text{Pd}_{0.80}$  is just a few per cent concentration below the jungle-gym disruption, as shown by the very broad peak just about L. ii) Along the  $\Lambda$  line, from  $\Gamma$  to L, there are two peaks. The sharpest measures the size of the electron octahedron, while the broadest is related with the jungle-gym.

On increasing  $c$ , CuPd undergoes various ETT's. While the reader is referred for details to our work about the isoelectronic system AgPd<sup>3</sup>, here we just observe that the d hole structure gets filled about  $c=0.60$ , as it is apparent when comparing the BSF's at  $c=0.55$  and  $c=0.60$ . Just above  $c=0.60$  the electron octahedron touches the Brillouin Zone border at the L point, as it is visible from the behaviours of the sharp peak along the  $\Gamma L$  line. At higher Cu contents, the noble metal-like neck is clearly visible (cfr. the two peaks along the KLU lines). The corresponding two ETT's, the opening of the neck at the L point and the closure of the d-hole at X, play a very important role in our discussion. The corresponding Van Hove singularities are a maximum (M) and a saddle point of index 2 (S2) in the dispersion relation,  $\epsilon = \epsilon(\vec{k})$  and the associated "critical" concentrations are listed in Table I.

As a function of  $c$ , CuPt exhibits similar ETT's. In this case, the BSF peaks appear broader than CuPd ones, namely due to relativistic effects. The analysis of the BSF's, however, shows us a much more remarkable difference: the neck opens at a lower  $c$  with respect to CuPd, as it is visible in Fig. 1 for  $\text{Cu}_{0.40}\text{Pt}_{0.60}$ , just above the critical concentration. Thus, while, in a narrow  $c$  interval, CuPd has the d-hole already filled and the neck not yet formed, the resulting FS being simply connected simple metal-like, this FS topology never occurs in CuPt. In Table I we report the relevant critical concentrations for both CuPd and CuPt and for the isoelectronic alloy AgPd, that, similarly to CuPd, presents a simple metal-like FS in a slightly larger concentration interval.

There is a relationship between these different behaviours of the above alloys in the random phase and the peculiarities of their phase diagrams mentioned in the Introduction. In order to show this, we need a little digression on the ETT theory. At  $T=0$ , neglecting the finiteness of quasi-

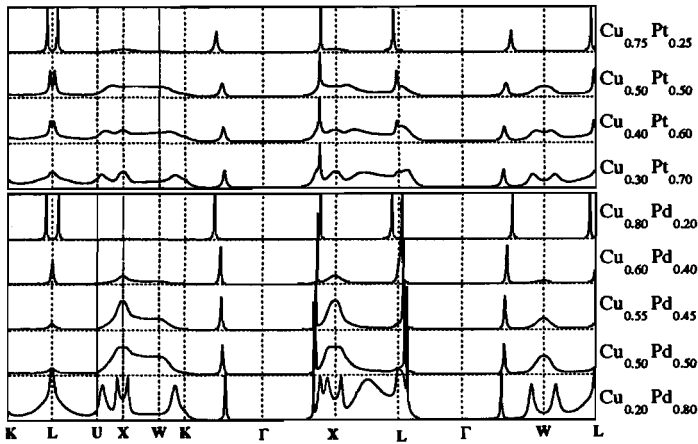


**Figure 1.** Calculated Bloch Spectral Function at the Fermi energy along high symmetry directions for CuPt and CuPd random alloys at the concentrations displayed in the figure.

particle lifetimes, the ETT-related contributions to the alloy free energy is a singular function<sup>3, 13</sup> of the chemical potential  $\mu$ ,

$$F_1(z) \propto -q|z|^{5/2} \Theta(z) \quad (1)$$

In eq. (1) the ETT “order” parameter  $z = s(\mu - \mu_c)$  measures, in a convenient direction, the chemical potential from that corresponding to the ETT. From the values given in Table I for the above  $s$  and  $q$ , we readily see that the occurrence of the ETT’s discussed in this paper always implies an increase of the alloy free energy. Thus, CuPt random alloys, that just below and above the equiatomic concentration present *both* the relevant ETT’s, are less stable than CuPd or AgPd and, thus more likely to be destabilised. Moreover, the proximity to both the critical concentrations implies large contributions to the BSF from the X and L points. Now, the concentration wave susceptibility,  $\chi_{cc}(\vec{q})$ , as observed by Gyorffy and Stocks<sup>8</sup>, is proportional to

$$\chi_{cc}(\vec{q}) \propto \int_{-\infty}^{\infty} d\epsilon \int_{-\infty}^{\infty} d\epsilon' \frac{f(\epsilon, T) - f(\epsilon', T)}{\epsilon - \epsilon'} \int_{BZ} d^3k A_B(\vec{k}, \epsilon) A_B(\vec{k} + \vec{q}, \epsilon') \quad (2)$$

where  $f(\epsilon, T)$  is the Fermi function. It is not difficult to show, in the low temperature limit, that a large contribution to the susceptibility comes from the self-convolution of the BSF at the Fermi level, say

$$\chi_{cc}(\vec{q}) \propto \int_{BZ} d^3k A_B(\vec{k}, \epsilon_F) A_B(\vec{k} + \vec{q}, \epsilon_F) \quad (3)$$

Thus, in the case of CuPt,  $\chi_{cc}(\vec{q})$  peaks in correspondence of the vector joining L and X, that is parallel to the (111) direction, *exactly* commensurate with the lattice and corresponds, in the direct space, to twice the distance between (111) planes. This is precisely the mechanism found by Clark et al.<sup>11</sup>.

**Table I.** The ETT’s discussed in this paper for CuPt, CuPd and AgPd<sup>3</sup> random alloys. The meanings of the various quantities reported are explained in the text.

| type | s  | q  | k-point | ETT critical concentrations |           |           |
|------|----|----|---------|-----------------------------|-----------|-----------|
|      |    |    |         | CuPt                        | CuPd      | AgPd      |
| M    | -1 | 1  | X       | 0.70±0.05                   | 0.60±0.05 | 0.53±0.05 |
| S2   | 1  | -1 | L       | 0.40±0.05                   | 0.65±0.05 | 0.70±0.05 |

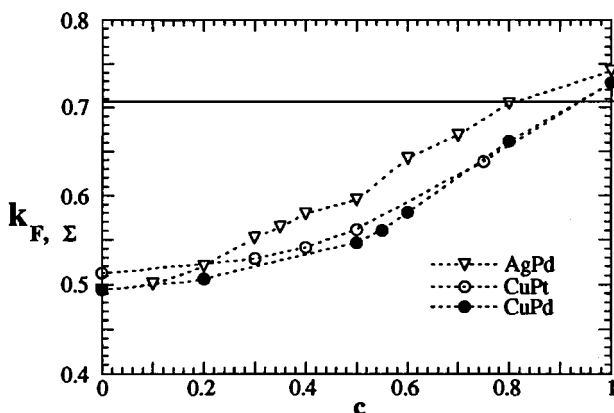


Figure 2. Calculated length of the Fermi wavevector along the  $\Sigma$  line,  $k_{F,\Sigma}$ , for AgPd<sup>3</sup>, CuPt and CuPd random alloys versus the noble metal atomic concentration,  $c$ . Dashed lines are drawn as a guide for the eyes. The solid line indicates the value,  $\sqrt{2}/2$ , at which  $k_{F,\Sigma}$  is exactly commensurate with  $L1_0$  or  $L1_2$  orderings.

In CuPd (and in AgPd), about  $c=0.50$ , the absence of states at the L point excludes the existence of FS contributions to  $\chi_{\alpha\alpha}(\vec{q})$  along (111). Smaller contributions, of course, could enter when considering the full eq. (2), that involves energy integrations. These, however would determine an ordering tendency toward the  $L1_1$  much smaller than for CuPt. Thus, an hypothetical  $L1_1$  phase could be found at very low temperatures, as Lu et al.<sup>14</sup> suggested it should be the case of AgPd.

The BSF's plotted in Fig. 1 allow us to discuss also ordering tendencies along the (110) direction. The electron octahedron centred at  $\Gamma$ , in fact, has large flat portions connected by the vector  $\vec{q} = 2\vec{k}_{F,\Sigma}$ , where  $\vec{k}_{F,\Sigma}$  is the distance from  $\Gamma$  of the peak along the  $\Gamma L$  line and is plotted, for all the alloys considered, in Fig. 2. On the basis of the eq. (2),  $\chi_{\alpha\alpha}(\vec{q})$  is expected to peak at the above wavevector. This is just a classical case of nesting and can be described by the KCM theory: in this case the concentration waves turn out to be commensurate with the lattice when  $2\vec{k}_{F,\Sigma} = (110)$ . This corresponds to structures with a periodicity equal to the lattice parameter along (100), and, that, depending on the stoichiometry, could be either  $L1_2$  or  $L1_0$ . As it is clear from Fig. 2, the above concentration waves can be commensurate only for Cu rich alloys. This explains the "asymmetry" of the experimental phase diagrams:  $L1_2$  ordering is observed, say, for Cu<sub>3</sub>Pd and Cu<sub>3</sub>Pt but not for CuPd<sub>3</sub> and CuPt<sub>3</sub>. On the other hand, we observe that, accordingly with Fig. 2, the concentration waves for CuPt and CuPd are exactly commensurate about  $c=0.90$ . This is in a reasonably good agreement with the known phase diagrams<sup>5</sup> that report the following critical points: ( $c=0.87$ ,  $T=781$  K) for  $L1_2$  CuPd and ( $c=0.84$ ,  $T=1008$  K) for  $L1_2$  CuPt. Closer to the stoichiometric concentration,  $c=0.75$ , LPS compatible with  $L1_2$  ordering are reported, as expected. Unfortunately, no low temperature data are available for AgPd, however, from our calculations one could expect for a  $L1_2$  phase, Ag<sub>3</sub>Pd, with a critical point closer than in CuPd and CuPt to the ideal stoichiometry.

Accordingly with Fig.2, at the equiatomic concentrations, the Fermi wavevector appears to be too far from being commensurate with the lattice for all the alloys considered in this paper. Thus, we are lead to exclude the occurrence of  $L1_0$  ordering and even LPS. However, about  $c=0.50$ , as a matter of fact, CuPd presents a B2 phase, based on a bcc lattice with a sequence of Cu and Pd planes along (100) and with a volume per atom about one per cent larger than in the fcc solid solution phase.

This suggests us a conjecture we think deserves to be explored further. We may think the bcc as a face centred lattice with a strong tetragonal distortion. In our case the atomic volume would be roughly conserved, thus the corresponding Brillouin Zone would result elongated in one direction and shrunk in the other two. As a result the twelve fcc {110} directions would separate into two equivalence groups, namely, along the eight tetragonal direction equivalent to (101), the Fermi wavevectors would increase their lengths. This could make the concentration waves more commensurate with the (new) lattice. This picture would imply a coupling between concentration and strain fluctuations and could explain the nature of this transition, that is, at the same time, order-disorder and martensitic.

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## **MECHANICAL PROPERTIES**

## STRUCTURE AND DEFORMATION OF Al-RICH TiAl SINGLE CRYSTALS

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### INTRODUCTION

TiAl possesses a wide composition range extending primarily on the Al-rich side and its mechanical properties strongly depend on aluminum content. The TiAl phase in equilibrium with the Ti<sub>3</sub>Al phase in TiAl/Ti<sub>3</sub>Al two-phase alloys has been found to be highly deformable [1-3]. However, the tensile ductility of the TiAl phase is quickly reduced to zero when aluminum content exceeds 53 at % Al [4]. Since the TiAl/(TiAl+Ti<sub>3</sub>Al) phase boundary is believed to be located at about 50 at% Al at room temperature, the drastic change in deformability occurs in a narrow composition range from 50 to 53 at% Al. To clarify the deformation behavior and mechanisms of Al-rich single-phase TiAl alloys, some basic studies have been done using single crystals [5-13]. In Al-rich alloys, ordinary slip on {111}<110>, superlattice slip on {111}<101> and twinning on {111}<112> can be operative depending on crystal orientation, similarly to the TiAl phase in TiAl/Ti<sub>3</sub>Al two-phase alloys. Some other slip systems can be operative, but they are observed only for very limited orientations and at temperatures higher than 1000°C. In view of the major deformation modes, no significant difference exists between the TiAl phase in two-phase TiAl alloys and the Al-rich TiAl phase. However, a remarkable difference exists in the relative ease of the three major deformation modes between the two TiAl phases with different Al contents. The relative ease of the three deformation modes in the former TiAl phase is given as

$$T_w > S_0 > S_s \quad (1)$$

while in the latter TiAl phase it is given as

$$S_s \gg S_0 \gg T_w, \quad (2)$$

where  $T_w$ ,  $S_0$  and  $S_s$  are the ease of twinning, ordinary slip and superlattice slip, and  $>$ ,  $\gg$

and >>> respectively indicate a small, a medium and a large difference in ease between the corresponding two deformation modes [3,12]. Such a drastic variation in the relative ease of the three deformation modes with Al content suggests that mechanisms of slip and twinning in the TiAl phase strongly depend on its Al content. Knowledge of the mechanisms would lead to understanding the reasons for the brittleness of the Al-rich TiAl phase and further to some new ideas for improving the mechanical properties of the TiAl phase in two-phase TiAl alloys which have been intensively studied for structural applications.

We have grown single crystals with compositions of Ti - 54 at% Al, Ti - 56 at% Al and Ti - 58 at% Al, and made a systematic study on their structure and deformation. In this paper we present the results of the systematic study reviewing some relevant previous studies.

## STRUCTURE OF Al-RICH CRYSTALS

Single crystals were grown from master ingots with nominal compositions of Ti - 54.0 at% Al, Ti - 56.0 at% Al and Ti - 58 at% Al using our ASGAL FZ-SS35W optical floating-zone furnace at a growth rate of  $5 \text{ mmh}^{-1}$  under an Ar gas flow. Hereafter we call these single crystals 54Al, 56Al and 58Al crystals, respectively. The composition of as-grown 56Al crystals was determined by wet chemistries to be Ti-55.95 at% Al with the major impurities of 250-300 wt.p.p.m. oxygen and 50-100 wt.p.p.m. nitrogen. The composition of 54Al and 58Al crystals is also expected to be very close to the corresponding nominal one with about the same amount of oxygen and nitrogen as in 56Al crystals.

Figures 1 (a)-(c) respectively show selected-area electron diffraction patterns taken along [001] of 54Al, 56Al and 58Al as-grown crystals. In addition to diffraction spots from the  $L1_0$  structure, some additional spots are observed in the patterns for 56Al and 58Al crystals, although additional spots for the former crystal are diffuse. Loiseau and Lasalmonie [14] have shown that Ti-Al alloys with compositions ranging from Ti - 56 at% Al to Ti - 63 at% Al have a heterogeneous structure constituted of island-like precipitates embedded in the matrix TiAl phase. The core of islands consists of a two dimensional long-period superlattice structure whose ideal composition is  $\text{Al}_5\text{Ti}_3$ . The  $\text{Al}_{11}\text{Ti}_7$  phase is considered to exist in the transition region between the core  $\text{Al}_5\text{Ti}_3$  phase and the matrix TiAl phase so that the transition region consists of a structure composed of a mixture of unit cells belonging to the  $\text{Al}_5\text{Ti}_3$  phase and the  $\text{Al}_{11}\text{Ti}_7$  phase.  $\text{Al}_5\text{Ti}_3$  and  $\text{Al}_{11}\text{Ti}_7$  phases have two-dimensional long-period superlattice structures which are closely akin and belong to the family of Ti-deficient TiAl ( $L1_0$  type) superlattice structures. Thus, the transition region has an intermediate average period depending on the size of island-like precipitates and leads to the incommensurability in diffraction patterns. Loiseau and Lasalmonie [14] have observed incommensurate as well as commensurate superlattice spots which have been interpreted very well in terms of the above mentioned heterogeneous structure.

The superlattice structure of  $\text{Al}_5\text{Ti}_3$  has been reported by Miida [15] and that of  $\text{Al}_{11}\text{Ti}_7$  has been proposed by Loiseau and Lasalmonie [14] to interpret the diffraction patterns obtained from Ti-Al alloys with compositions ranging from Ti - 56 at% Al to Ti - 63 at% Al. Unit cells of the two superlattice structures are shown in Fig.2(a) and (b) together with the unit cell of the TiAl phase. The TiAl ( $L1_0$  type) structure is a fcc-based tetragonal superlattice structure where cube planes occupied exclusively by either Ti or Al atoms alternately stack along the tetragonal axis. In  $\text{Al}_5\text{Ti}_3$  and  $\text{Al}_{11}\text{Ti}_7$  superlattice structures, Ti atoms of Ti planes of the TiAl structure are regularly replaced by Al atoms. Depending the

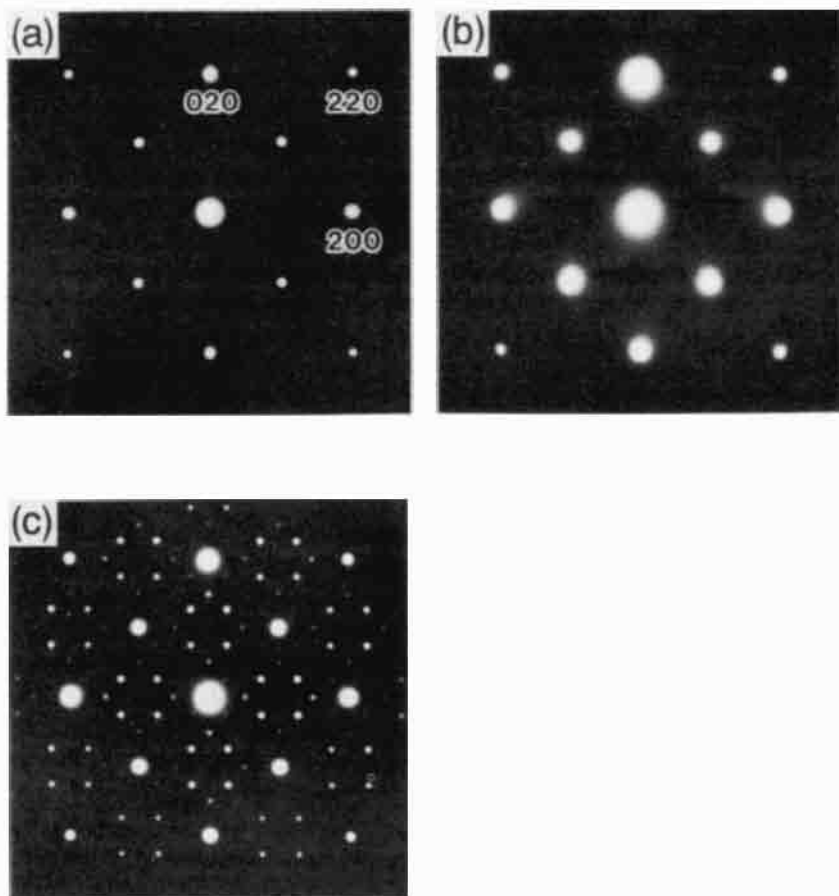


**Figure 1.** SAED patterns taken from as-grown (a) Ti-54 at.%Al, (b) Ti-56 at.%Al and (c) Ti-58at.%Al single crystals along [001].

regular arrangement of such excess Al atoms,  $\text{Al}_5\text{Ti}_3$  and  $\text{Al}_{11}\text{Ti}_7$  superlattice structures have lattice parameters shown in Fig.2(a) and (b). As has been shown by Loiseau and Lasalmonie [14], when [001] atomic rows composed only of Al atoms are plotted, the two superlattice structures can be represented by a combination of squares and lozenges (Fig.2(a-c)). Commensurate diffraction patterns for  $\text{Al}_5\text{Ti}_3$  and  $\text{Al}_{11}\text{Ti}_7$  superstructures are shown in Fig.2 (d) where large solid, small solid and small open circles represent spots characteristic of the TiAl,  $\text{Al}_5\text{Ti}_3$  and  $\text{Al}_{11}\text{Ti}_7$  phases, respectively [14]. Diffraction from the transition regions with an intermediate composition between  $\text{Al}_5\text{Ti}_3$  and  $\text{Al}_{11}\text{Ti}_7$  produces diffraction spots at incommensurate positions deviated from corresponding commensurate  $\text{Al}_5\text{Ti}_3$  spots by  $\delta$  which is in the range of  $0 < \delta < \delta_0$  (Fig.2(d)). Such incommensurability is clearly seen in the diffraction pattern of Fig.1(c), and in fact we have confirmed a heterogeneous structure such as that observed in 63Al alloy by Loiseau and Lasalmonie [14].

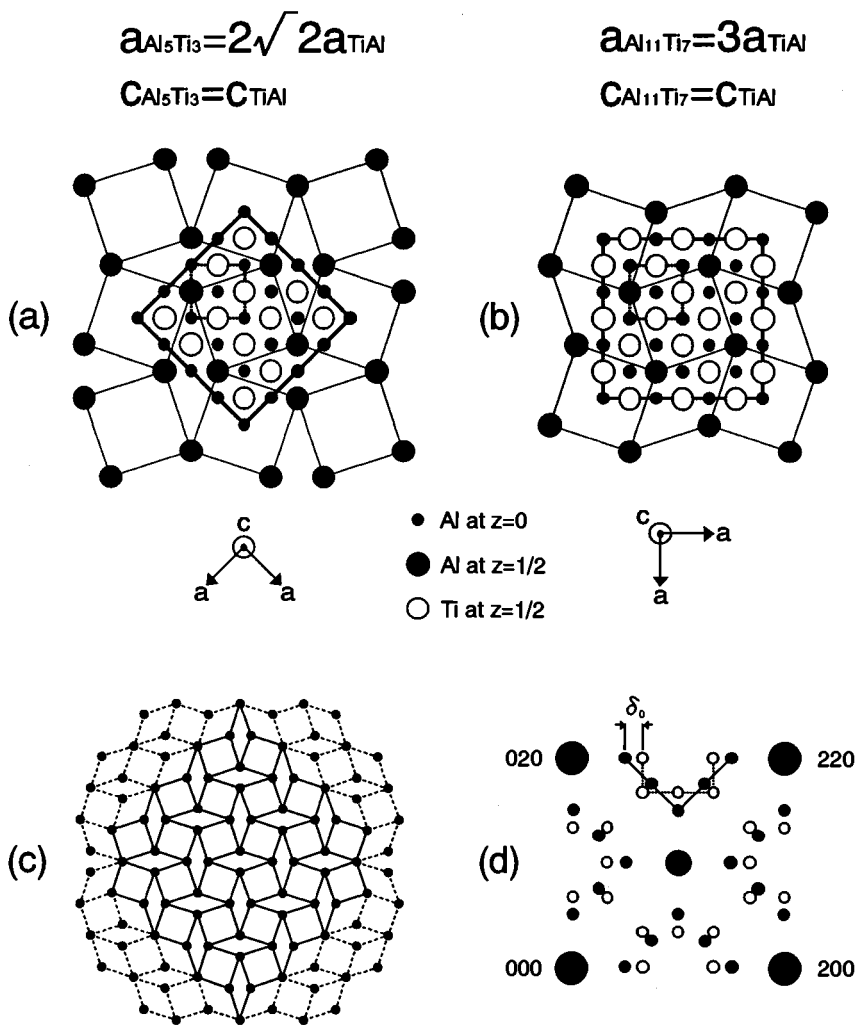


**Figure 2.** (001) projection of (a)  $\text{Al}_5\text{Ti}_3$  and (b)  $\text{Al}_{11}\text{Ti}_7$  structures. A model for island-like precipitates composed of the core  $\text{Al}_5\text{Ti}_3$  phase and the periphery  $\text{Al}_{11}\text{Ti}_7$  phase is shown in (c), and (d) shows a schematic illustration of commensurate  $\text{Al}_5\text{Ti}_3$  (small solid circles) and  $\text{Al}_{11}\text{Ti}_7$  (small open circles) diffraction patterns [14].

Figures 3 (a) and (b) show typical examples of high resolution electron microscope (HREM) images taken from thin foils prepared from 56Al and 58Al crystals at low and high magnifications. The HREM image for the 56Al crystal appears to be homogeneous, while in the 58Al crystal some island-like precipitates such as those marked by P in the lower magnification image can clearly be recognized. The strongly bright spots correspond to the atomic rows composed of Al atoms only. The combination of squares and lozenges characteristic of the  $\text{Al}_5\text{Ti}_3$  superlattice structure is seen in the higher magnification image which was taken from one of island-like precipitates. Loiseau and Lasalmonie [14] reported

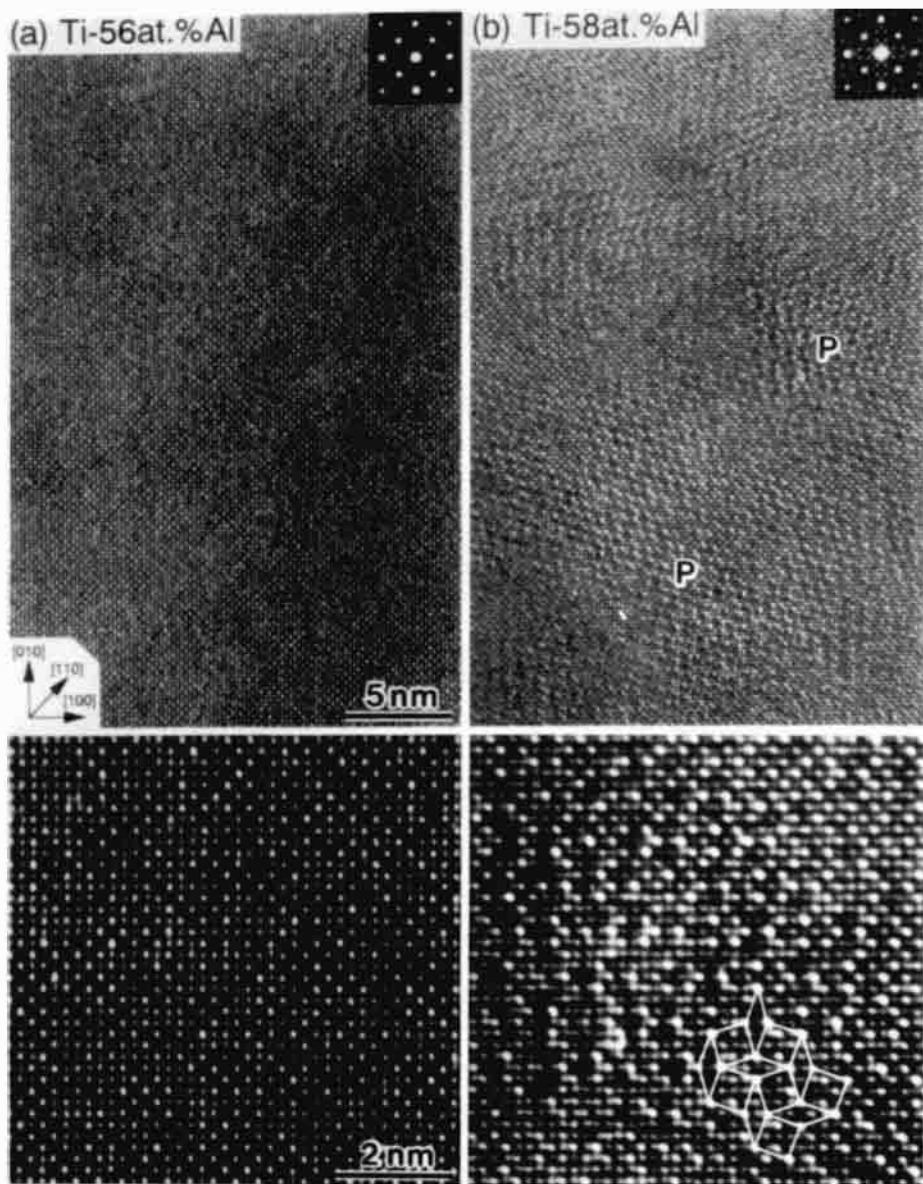


**Figure 3.** HREM images of (a) Ti-56at.%Al and (b) Ti-58at.%Al crystals taken along [001].

that such a diffraction pattern as that shown in Fig.1(c) was observed in Ti-Al alloys with compositions in the range of 56Al - 63Al. We observed diffraction spots corresponding to the Al<sub>5</sub>Ti<sub>3</sub> superlattice structure in the 56Al crystal, however, they are diffuse and rather weak. Hug [16] ascribed the occurrence of such diffuse additional spots in 56Al alloy to the Al<sub>5</sub>Ti<sub>3</sub>-type short-range ordering of Al atoms existing in excess of the stoichiometric composition of TiAl. Our experimental results seem to support him. In fact, no microstructural heterogeneity such as that found in Fig.3(b) is observed in the HREM image of Fig.3(a). The composition range where the Al<sub>5</sub>Ti<sub>3</sub> phase is observed may depend on the

impurity species and their amount and the conditions of alloy preparation such as cooling rate and annealing temperature. In 54Al crystal, even the  $\text{Al}_5\text{Ti}_3$ -type short-range ordering of Al atoms does not exist as seen in Fig.1(a).

## DEFORMATION MODE AND CRITICAL RESOLVED SHEAR STRESS

Specimens for compression tests with various orientations, measuring 2.5 mm x 2.5 mm in cross-section and 6 mm length, were cut from 54Al and 56Al as-grown crystals by a spark-cutting machine. Such specimens were polished first mechanically and then electrolytically prior to mechanical testing. Orientations of crystals were determined by the X-ray back-Laue diffraction method after differentiating (001) from {100} by electron diffraction. Compression axis orientations investigated were [001],  $[\bar{1}52]$ , [021],  $[\bar{2}51]$ ,  $[\bar{2}33]$ ,  $[\bar{1}91]$  and  $[\bar{1}10]$  for 56Al crystals and [001],  $[\bar{1}52]$  and [021] for 54Al crystals in the [001]- $[\bar{1}10]$ -[010] unit triangle. Compression tests were carried out on an Instron-type testing machine at a strain rate of  $2 \times 10^{-4} \text{ s}^{-1}$  in the temperature range of -196~1100°C. Tests above room temperature were made in vacuum while those at -100°C and -196°C were conducted immersing specimens in ethanol chilled with liquid nitrogen and in liquid nitrogen, respectively. Deformation structures were examined by optical and transmission electron microscopy.

The deformation modes observed in 56Al crystals at temperatures from liquid nitrogen temperature to 1100°C are ordinary slip on {111}<110], superlattice slip on {111}<101], twinning on {111}<112] and slip on some other slip systems such as {111}<112], (001)<110] and {110}<110] [13]. The temperature and crystal orientation dependence of the CRSS for these deformation modes is shown in Fig.4 [13]. At low temperatures, the strength of 56Al crystals rapidly decreases with increasing temperature up to around room temperature and then stays almost constant up to 600°C. Above 600°C, the strength increases anomalously with temperature exhibiting a peak at 600-1000°C depending on crystal orientation, then followed by a rapid decrease at high temperatures. A similar behavior has been reported on single crystals [5,9,10,17] and polycrystals [18,19] of Al-rich single-phase TiAl alloys.

The deformation modes observed below the peak temperature region are ordinary slip on {111}<110] and superlattice slip on {111}<101]. The CRSS for <101] superlattice slip depends strongly on crystal orientation and the Schmid's law does not hold, although the reasons for this has yet to be clarified. Whether or not the Schmid's law is valid for <110] ordinary slip is not yet clear. It is rather difficult to investigate the orientation dependence of the CRSS of <110] ordinary slip since the orientation range where <110] ordinary slip is operative is very limited because of the large difference in CRSS between <110] ordinary and <101] superlattice slip. In fact, below the peak temperature <101] superlattice slip is the primary deformation mode for most orientations except those near [021] in the [001]- $[\bar{1}10]$ -[010] unit triangle [13]. An anomalous increase in CRSS is seen to occur for both slip systems at intermediate temperatures. An anomalous strengthening mechanism similar to that in  $\text{Ni}_3\text{Al}$  is likely to be operative, as was suggested in previous studies on the deformation of TiAl [7,9,13,16]. However, more work is needed to make out the similarities and differences in the anomalous strengthening mechanism between TiAl and  $\text{Ni}_3\text{Al}$ . Our recent work on the anomalous strengthening mechanism and relevant dislocation structures will be described elsewhere in detail [20]. A model for the strength anomaly for <110] ordinary slip has been proposed by Louchet and Viguier [21] based on observations of dislocations by Viguier et al. [11].

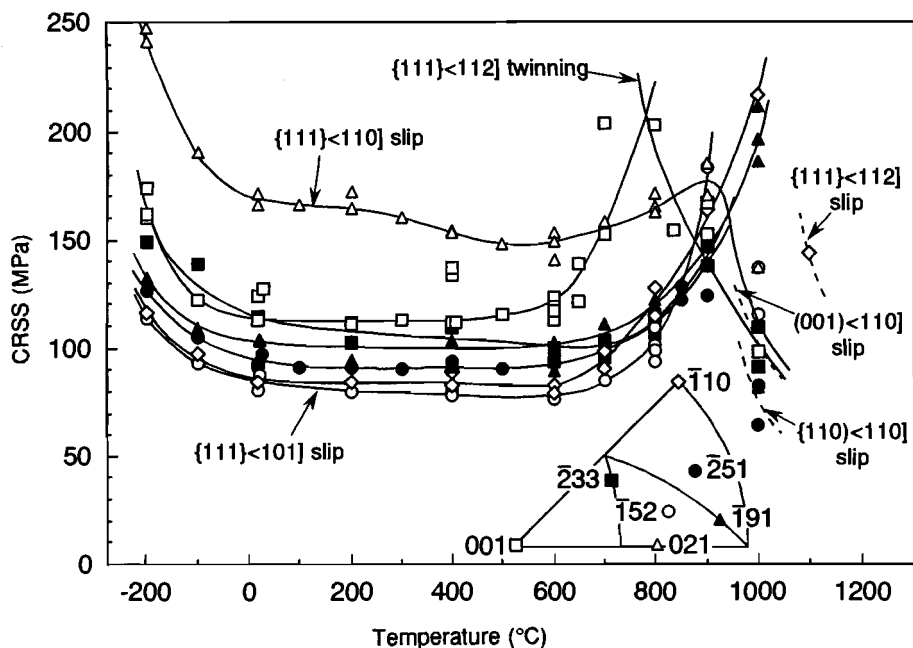


**Figure 4.** Temperature dependence of CRSS for the six different deformation modes observed in Ti-56 at.%Al single crystals.

Above the anomalous peak temperature,  $\langle 110 \rangle$  ordinary slip, twinning and  $\langle 112 \rangle$  slip are operative depending on crystal orientation.  $\langle 110 \rangle$  ordinary slip occurs not only on  $\{111\}$  but also on  $\{001\}$  and  $\{110\}$ . Superlattice slip along  $\langle 101 \rangle$  is never observed above the peak temperature. This is in contrast to  $\text{Ni}_3\text{Al}$  where a slip plane transition from  $\{111\}$  to  $\{010\}$  occurs around the anomalous peak but the slip direction  $\langle 101 \rangle$  remains unchanged. The CRSS for  $\langle 110 \rangle$  slip and twinning decreases rapidly with increasing temperature. This should be the case also for  $\langle 112 \rangle$  slip, although nothing is known about the temperature dependence of the CRSS for the slip because of the limited orientation and temperature range for its operation. In the following three paragraphs, dislocation structures and the results of related observations for some typical orientations are briefly summarized based on our recent work [13].

For  $[001]$  and  $[\bar{1}10]$  orientations where no stress is resolved onto  $\langle 110 \rangle$  ordinary slip,  $\langle 101 \rangle$  superlattice slip is observed up to the peak temperature.  $\langle 101 \rangle$  dislocations predominantly lie along their screw orientation up to the peak temperature. This is consistent with the recent results of TEM observations on  $[001]$  single crystals by Stucke et al. [9]. At temperatures below the peak, CRSS is much higher for the  $[001]$  orientation than for the  $[\bar{1}10]$  orientation. However, both the peak temperature and peak stress are lower for the former orientation than the latter. The lower peak temperature for the  $[001]$  orientation is associated with the occurrence of twinning of the  $\{111\}\langle 112 \rangle$ -type above the peak temperature. Such twinning can not occur for the  $[\bar{1}10]$  orientation in compression. Deformation of  $[\bar{1}10]$ -oriented crystals above the peak is carried by slip on  $\{111\}\langle 112 \rangle$ .

For the  $[\bar{1}52]$  orientation, where the resolved shear stress for  $\langle 110 \rangle$  ordinary slip is 1.3 times that for  $\langle 101 \rangle$  superlattice slip,  $\langle 101 \rangle$  superlattice slip is observed up to the peak temperature. Above the peak,  $\langle 110 \rangle$  ordinary slip occurs mostly on  $\{111\}$ . Near the peak temperature,  $\langle 101 \rangle$  dislocations are mostly in their screw orientations with many



superkinks, as previously reported [7,9,22]. Their fine structures will be described in detail in [20].

For the [021] orientation, where the resolved shear stress for <110] ordinary slip is twice that for <101] superlattice slip, <110] ordinary slip is observed in the whole temperature range. Hence the profile of the CRSS versus temperature curve for this orientation, including the strength anomaly, is solely associated with <110] ordinary slip. The peak in CRSS is observed at 900°C. However, the peak height is seen to be very small when compared to those for other orientations where the anomaly is associated with <101] superlattice slip. Ordinary dislocations with  $b = 1/2<110]$  tend to be parallel to their screw and 60° orientations at low temperatures, whereas they are roughly in the screw orientation and accompanied by many cusps near the peak temperature [13]. Tilting experiments have indicated that cusps are not on the primary slip plane but are bowed-out on different planes, indicating the frequent occurrence of cross-slip. Such dislocation structures seem to be in agreement with those observed by Viguier et al. [11] and Bird et al. [10].

### ALUMINUM CONCENTRATION DEPENDENCE OF CRITICAL RESOLVED SHEAR STRESS

The CRSS for <110] ordinary and <101] superlattice slip and twinning of the {111}<112] type for 56Al and 54Al crystals is plotted as a function of temperature in Fig.5. The trend of the results for 54Al crystals is very similar to that of the results for 56Al crystals. The CRSS for the three deformation modes is generally lower for 54Al crystals than for 56Al crystals. Interestingly, the decrease in CRSS caused by a decrease in Al

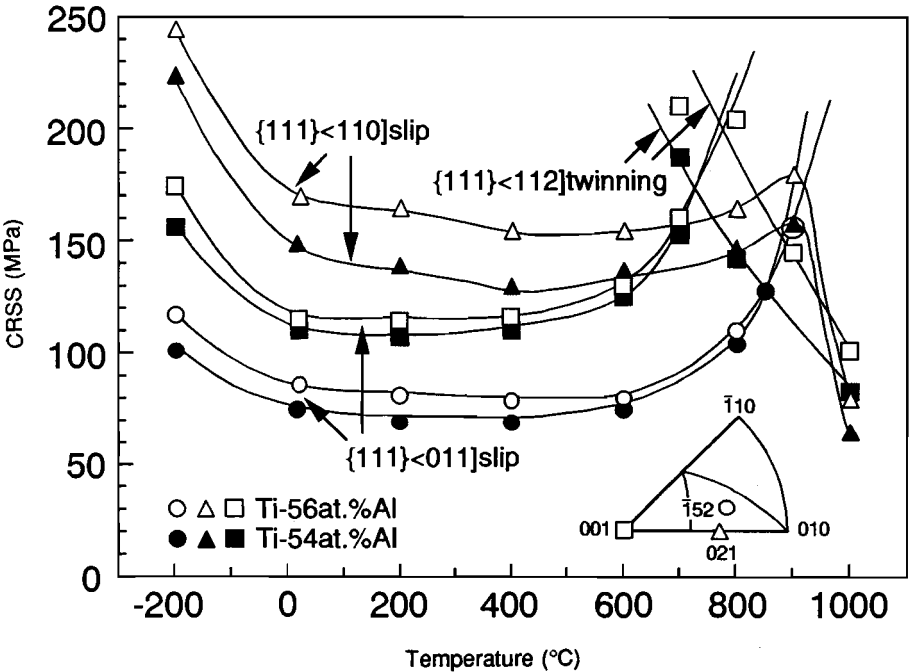


**Figure 5.** Temperature dependence of CRSS for <101] superlattice slip, <110] ordinary slip and twinning observed for Ti-54 at.%Al and Ti-56 at.%Al single crystals.

content by 2 at% is much larger for  $\langle 110 \rangle$  ordinary slip than for  $\langle 101 \rangle$  superlattice slip. Thus, the difference in CRSS between  $\langle 110 \rangle$  ordinary and  $\langle 101 \rangle$  superlattice slip is expected to be considerably reduced at 50 at% Al. In fact, the difference in case between the three deformation modes in the TiAl phase in equilibrium with the  $\text{Ti}_3\text{Al}$  phase is so small that the hardest mode ( $\langle 101 \rangle$  superlattice slip) often coexists with the easiest mode (twinning) and/or the second easiest mode ( $\langle 110 \rangle$  ordinary slip) in the TiAl phase in deformed two-phase TiAl alloys. On top of that, when the CRSS values for  $\langle 110 \rangle$  ordinary and  $\langle 101 \rangle$  superlattice slip for 56Al and 54Al crystals at room temperature are extrapolated towards 50 at% Al, we obtain the values somewhat close to the CRSS values for the two slip modes in the TiAl phase in two-phase TiAl alloys at room temperature [13]. The CRSS values for the TiAl phase in two-phase TiAl alloys are estimated from the yield stress of PST crystals with B orientation [1,3]. Twinning is not observed at room temperature in 54Al and 56Al crystals. However, extrapolation of the CRSS values for twinning in the two crystals at 800°C back to 50 at% Al yields a value close to the CRSS for twinning in the TiAl phase in PST crystals at 800°C. This suggests that the mechanical properties of the TiAl phase vary with its Al content in a continuous manner at least up to 56 at% Al rather than in an abrupt way at a certain critical Al content. However, the mechanism of the Al content dependence of mechanical properties of the TiAl phase has yet to be clarified.

## EFFECTS OF SHORT-RANGE ORDERING OF EXCESS Al ATOMS

The results for 54Al and 56Al crystals shown in Fig.5 show the same trend, although the  $\text{Al}_5\text{Ti}_3$ -type short-range ordering of the lattice exists in 56Al crystals and does not in 54Al crystals. We may thus draw a conclusion that the short-range ordering of the lattice in 56Al crystals may not exert any decisive influence on the general trend of the temperature and crystal orientation dependence of deformation modes and their CRSS. However, the short-range ordering must have some effects on the deformation of 56Al crystals. Figure 6 shows an example of such effects [13]. As seen in Fig.6(b), ordinary dislocations with  $b = 1/2\langle 110 \rangle$  tend to occur in groups, each of which consists of four dislocations in most cases. A similar behavior has been observed in [16,23,24], and Hug[16] has interpreted the dislocation behavior in terms of the short-range ordering of the lattice. In contrast to 56Al crystals, such dislocation behavior has not been observed in 54Al crystals. Figure.6(a) shows a typical dislocation structure observed in a  $[021]$ -oriented 54Al crystal deformed at room temperature. They tend to align along their screw orientation, but do not show any tendency to occur in groups. However, the implications of such observations for the strength of 56Al crystals have yet to be clarified.

Recently, some attempts have been made to understand the deformation behavior of TiAl from the point of view of dislocation core structures and their behavior under the effect of an applied shear stress [26-28]. Vitek and his colleagues have suggested that the most important factor controlling the deformation modes in TiAl is the dependence of the superlattice intrinsic stacking fault (SISF) and twin boundary energy on the Al concentration. The results of their dislocation core calculations may provide a basis for understanding the Al concentration dependence of the deformation modes in the TiAl phase if it is assumed that the energies of both the SISF and the coherent twin boundary increase rapidly with increasing Al concentration. The assumption seems to be the case [29,30]. In fact, the ease of twinning drastically decreases with increasing Al concentration (see eqs. (1) and (2)), and dislocations widely dissociated involving SISF are often observed in the TiAl phase in deformed PST crystals [3], but not in Al-rich single-phase TiAl crystals [13].

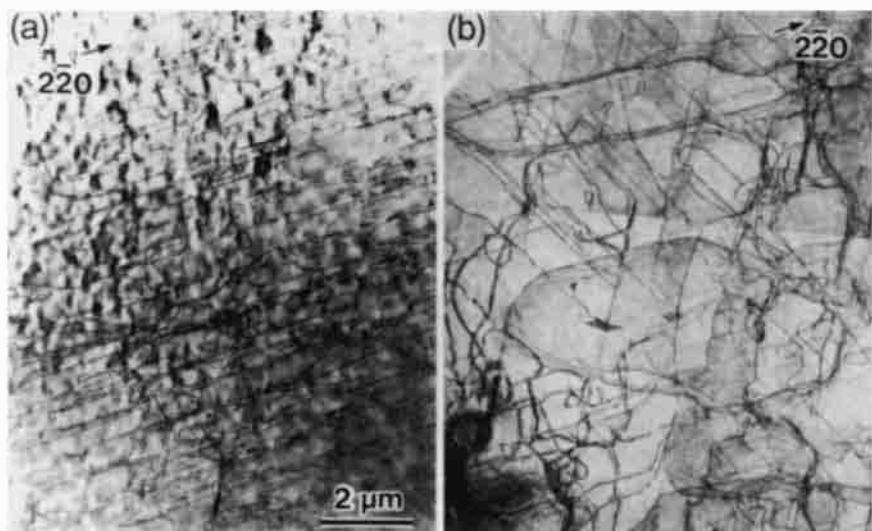


**Figure 6.** Dislocation structures observed in (a) Ti-54 at.%Al and (b) Ti-56 at.%Al crystals with the [021] orientation deformed at room temperature.

However, it is not yet clear why the energies of the SISF and the twin boundary increase with increasing Al concentration. To find a clue to the problem, it would be needed to make out the effects of the short-range ordering of Al atoms in excess of the stoichiometric composition of the TiAl phase on the energies of planar faults and the structure of dislocation cores in the Al-rich TiAl phase.

## CONCLUSIONS

In this paper we have presented recent studies on the structure of 54Al, 56Al and 58Al crystals and the deformation of 54Al and 56Al single crystals. Island-like precipitates of the  $\text{Al}_5\text{Ti}_3$  phase was observed in 58Al crystals and some incommensurability was found in electron diffraction patterns of 58Al crystals. The  $\text{Al}_5\text{Ti}_3$ -type short-range ordering of excess Al atoms exists in 56Al crystals. No evidence for such short-range ordering of excess Al atoms was found in 54Al crystals.

In comparison to the deformation of PST crystals in which the TiAl phase coexists with the  $\text{Ti}_3\text{Al}$  phase in the lamellar form [1-3], the most remarkable features in the deformation of 54Al and 56Al single crystals are summarized as follows: (i) the relative ease of slip and twinning increases in the sequence of twinning,  $\langle 110 \rangle$  ordinary slip and  $\langle 101 \rangle$  superlattice slip below  $600^\circ\text{C}$ , whereas in PST crystals, it increases in the reversed sequence and (ii) twinning is observed only at temperatures higher than  $800^\circ\text{C}$  and its CRSS exhibits a very strong temperature dependence.

In view of that the trend of the temperature and orientation dependence of the deformation modes and their CRSS for 54Al crystals is the same as for 56Al crystals, the influence of the short-range ordering of excess Al atoms seems not to be such that the basic features of deformation of the Al-rich TiAl phase are altered depending on whether the short-range ordering of excess Al atoms exists or not. However, the short-range ordering must exert some influences on the deformation of 56Al single crystals. For example, the occurrence of  $1/2\langle 110 \rangle$  ordinary dislocations in groups, which is thought to be an evidence

of the short-range ordering of the lattice, was observed in a deformed 56Al single crystal. The implications of the short-range ordering of the lattice for the deformation of 56Al single crystals has yet to be studied.

## ACKNOWLEDGMENTS

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## EXPERIMENTAL STUDIES ON PRECURSOR PHENOMENA IN DISPLACIVE PHASE TRANSFORMATIONS

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### INTRODUCTION

It has been known for quite a long time that many first order transformations are preceded by a number of different precursing phenomena in the parent phase. These phenomena can be observed by experiments probing at the macroscopic as well as microscopic level. In the present contribution we will take a closer look at the relative relations between different precursor phenomena and also with the ensuing phase transformations. In practice we will limit ourselves to displacive phase transformations with the emphasis on martensitic transformations. Although the increasing amount of experimental data and recent refinements in theoretical models indicate clear connections between most precursors in a given system, the question whether or not these precursors have any specific effect on the final structure or configuration of the product phase still remains, however.

Among the first macroscopic observations of this type one can count the changes in certain elastic constants when approaching the martensitic transformation temperature  $M_s$ . Measurements of this type are still continued and currently provide data of a broad range of materials. Also acoustic measurements and thermal expansion experiments are these days conducted with the aims of obtaining new insight into the macroscopic aspects of the precursor mechanisms. Microscopic data, on the other hand, is primarily found by the different variants of elastic or inelastic scattering experiments, using the typical x-ray, neutron or electron probes and yielding reciprocal space figures. The information obtained from the first two is averaged over the entire sample volume or at least a size much larger than the aimed microscopic level. The use of electrons, however, also enables one to obtain real space images down to the atomic scale of the region from which the diffraction is formed. In all of these cases in-situ work is of course preferred as it yields direct information on the transformation path.

Instead of listing results of all these different experiments on the large variety of possible materials we will focus on some case studies which might serve as model systems for a given

group of phase transformations. In the present contribution the body centred cubic to close packed phase transformations were chosen for this purpose. Recent overviews on different aspects of precursor phenomena specifically with respect to martensitic transformations were written by Nagasawa & Morii<sup>1</sup> and Pushin & Kondrat'ev<sup>2</sup>. One such system, which has been thoroughly studied experimentally as well as theoretically in the past is that of the body centred cubic to face centred tetragonal martensitic transformation in Ni-Al. Recently new but very similar data on precursor phenomena in related systems such as Ni-Mn-Ti and Ni-Mn-Ga (Heusler-type) alloys has been obtained and will be compared to the previous results on Ni-Al. Going down to the details of the atomic structures will enable us to correlate the results of different experimental techniques and to interpret them in the view of recent theoretical models.

## PRECURSORS OF MARTENSITIC TRANSFORMATIONS

One of the more recent definitions of a martensitic transformation is that of a "shear-dominant, lattice-distortive, diffusionless transformation occurring by nucleation and growth"<sup>3</sup>. This means that the transformation starts at one or more nucleation points in the parent or austenite phase and the product or martensite structures, which often appear in typical morphological shapes such as plates or rods, will grow at the expense of the parent phase. At any given time during this transformation process, which can be athermal or isothermal, the austenite and martensite regions will be separated by a well defined interface or habit-plane. The actual change in atomic structure reflects a distortion of the basic lattice - opposite to shuffle transformations in which the contours of a given unit remain fixed - and is primarily driven by a shear or deviatoric component. The diffusionless character implies that the short as well as long range ordering remains unchanged. As the concept of a nucleation and growth mechanism is essential, martensitic transformations belong to the group of first order transformations. Its first order character, however, can be strong, moderate or weak.

In all of this, the idea of precursor phenomena is not essential. In principle the austenite could remain undistorted - except for a normal lattice contraction when decreasing temperature - upto the transition point. Nevertheless, in many systems undergoing a moderate or weak first order martensitic transformation anomalous behaviour when approaching the transition temperature has been detected by different experimental techniques. This, however, does not immediately imply any correlation whatsoever with the ensuing transformation, let alone being a necessity for the latter. Still, more and more phenomena of this nature are detected for a wider range of materials and the search for actual correlations with the martensitic transformation and structure shows some interesting evolutions. Also in the larger field of displacive transformations in general similar examples exist.

### BCC to Close Packed

One group of martensitic transformations is that in which the austenite or parent structure is based on a body centred cubic (bcc) lattice, usually referred to as the  $\beta$  phase. For binary alloys this lattice is often ordered in the B2 (CsCl) or DO<sub>3</sub> (Fe<sub>3</sub>Al) configurations whereas ternary alloys often exhibit the L2<sub>1</sub> Heusler-type (Cu<sub>2</sub>MnAl) ordering<sup>4</sup>. Depending on the actual system the martensite structure can be close packed, with a possibility for multiple and periodic microtwinning or stacking faults, or complex with a low symmetry. Examples of the former include Ni-Al and Ni-Mn as well as their ternary derivatives in which the actual stacking or microtwin sequences strongly depend on composition. Also some Cu-based alloys exhibit close packed sequences for the martensite. Au-Cd, Au-Zn and Ni-Ti belong to the second type.

When the austenite is ordered with the B2 structure and the martensite is of the close packed type the latter is based on a face centred tetragonal (fct) lattice with an  $L1_0$  type ordering as a direct result of the diffusionless character. The transformation can be described by different geometrical constructions, one being a simple tetragonal distortion during which one of the bcc cubic axes is elongated, the other two being equally compressed. Alternatively, the combination of a homogeneous shear of the  $(1\bar{1}2)$  planes in the  $[\bar{1}11]$  direction together with a specific shear or shuffle of the  $(110)$  planes in the  $[1\bar{1}0]$  direction can also yield the same martensite structure<sup>4</sup>. The first one is necessary to obtain close packed planes in the martensite while the second one arranges these planes in a given stacking and thus corresponds with the possibility of multiple twinning or stacking faults on these planes. Shearing in the same direction for every  $(110)$  plane yields an ABC stacking while opposite shears result in an ABAB stacking and are sometimes called shuffles. In view of the close packed nature of the final basal planes the resulting lattice is described in fct rather than body centred tetragonal (bct) terms. By using the latter approach the distortions can be correlated with physical features of the austenite such as the lattice softening of the  $C' = (C_{11} - C_{12}) / 2$  shear modulus or the overall low energy of the  $TA_2[110]$  phonon branch. Both are related with the homogeneous  $(110)[1\bar{1}0]$  shear and display remarkable anomalous behaviour close to but clearly above the transformation temperature. A typical precursor feature of the phonon dispersion curve is a dip at a given frequency, correlated with a shuffle of the corresponding wavelength, whereas for the elastic constants a strong increase in anisotropy is noted. At the same time elastic scattering can reveal  $[110]$  diffuse intensity around the Bragg peaks or reflections, sometimes even with a distinct satellite. The extinction conditions, corrected for double diffraction in the case of dynamic scattering, indicate that this diffuse intensity with its possible satellite correspond with  $(110)[1\bar{1}0]$  transverse displacement waves. The tweed patterns in conventional two-beam transmission electron microscopy (TEM) indicate that these displacement waves have a static character. The effects of the satellite can only be visualised by using high resolution TEM (HRTEM) and will be discussed further on.

In the case of Ni-Al the martensitic transformation occurs in a composition range between 62 and 67 at.% Ni where the excess Ni is accommodated randomly on the Al sublattice<sup>5</sup>. The resulting  $c/a$  ratio of the  $L1_0$  structure is around 0.85, depending on composition. Below 63 at.% Ni the martensite structure has a  $(5\bar{2})$  sequence of close packed planes<sup>6</sup> (Zhdanov notation) which is currently denoted as  $14M$ <sup>7</sup> (formerly as  $7R$ ). At higher Ni contents this typical sequence is lost and the martensite plates are simply internally twinned without a specific periodicity.

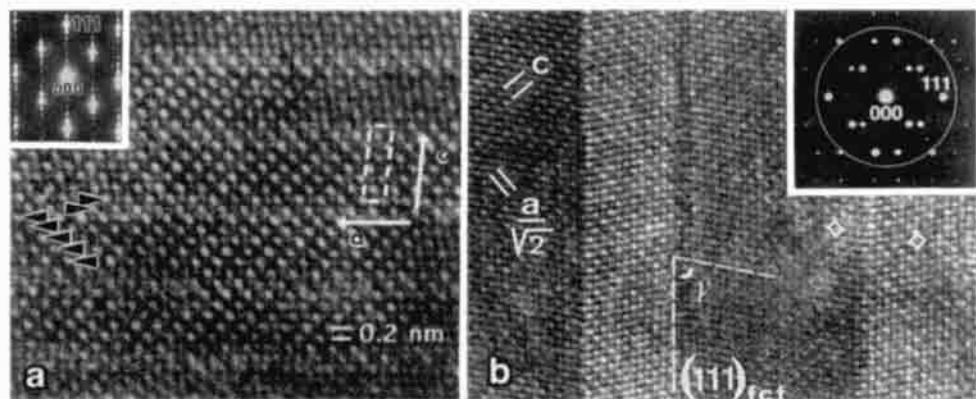


Figure 1: HRTEM images of the (a)  $14M$  and (b)  $L1_0$  martensite in Ni-Al including the corresponding SAED patterns.



Figure 1 shows HRTEM images of both cases, 14M and L1<sub>0</sub> twinned, as well as the corresponding [1 $\bar{1}$ 0] selected area electron diffraction (SAED) patterns, that of the former clearly revealing 6 superreflections in the [111]<sub>fcc</sub> direction<sup>8</sup>. The pattern of white dots in the HRTEM images reflects the projected configuration of the atomic columns in this zone<sup>9</sup> immediately resulting in a direct recognition of the twinning. In Ni-Mn the martensite appears around the equiatomic composition with an even broader variety of stacking sequences depending on composition<sup>10</sup>.

HRTEM images of the austenite but taken very close to the transformation temperature reveal the static atomic configurations corresponding with the precursors. In figure 2a and 2b examples are given of the situation close to the 14M and to the L1<sub>0</sub> transformation, respectively. In both cases the austenite consists of a contiguous patchwork of distorted domains of approximately 5 nm in diameter, sometimes referred to as “inhomogeneously strained domains” or ISD’s. The average lattice remains cubic which is reflected in the strong Bragg reflections of the SAED patterns. The most important difference between the two cases is that for the 14M precursor these ISD’s are internally modulated by a transverse (110)[1 $\bar{1}$ 0] shuffle displacement wave, a so-called micro-modulation. Extensive image simulations have indicated that the actual modulated contrast inside these domains can be explained by superposing this displacement wave onto an inhomogeneous deformation which should be maximum in the centre of the domain and die out towards its edges<sup>11</sup>. The averaged wavelength of the micro-modulation is incommensurate and between 6 and 7 (110)<sub>bcc</sub> planes. The domains in the L1<sub>0</sub> precursor are clearly not internally modulated. They reveal a clear white dot pattern or a line pattern along two possible <100> directions. The latter effect can be attributed to the inhomogeneous strain itself in a direction inclined to the surface, thus disturbing the perfect column structure necessary for the appearance of the white dots<sup>9</sup>. The fact that these distortions can be photographed in a HRTEM indicate that they have a static nature. Both cases result in diffuse <110> scattering around the Bragg reflections in reciprocal space plus a satellite in the case of the micro-modulation (arrows in inset of 2a).

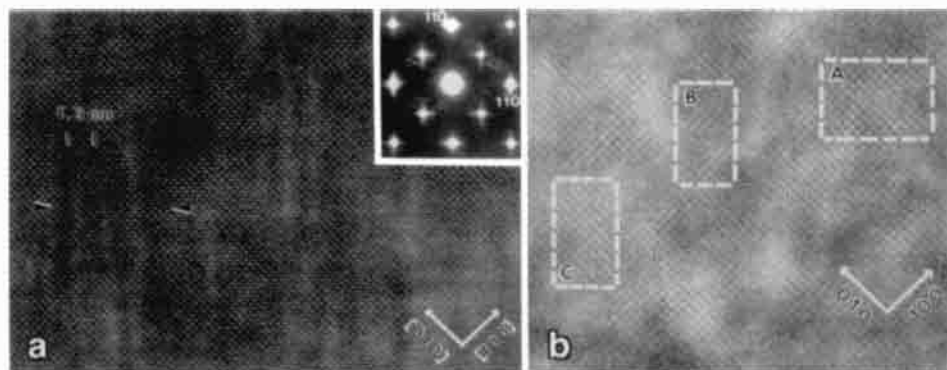


Figure 2: [001] HRTEM images of the austenite with static precursor distortions observed prior to the (a) 14M and (b) L1<sub>0</sub> transformation in Ni-Al<sup>11</sup>. The position of the satellite for (a) is indicated in the inset.

When comparing the HRTEM images of the precursor distortions in figure 2 with the stacking sequences of the martensite in figure 1 it is seen that both martensite structures are preceded by local distortions in all possible variants and mimicking, although with smaller amplitudes, the final shears and shuffles necessary to produce the proper stacking of close packed planes of the martensite. This is especially apparent in the case of the 7 close packed layer stacking of the 14M structure which is preceded by a micro-modulation with a

wavelength of appr. 1.3 nm. Unfortunately, due to the resolution limits in the case of changing temperature, the actual evolution between the two situations cannot, as yet, be followed in-situ with HRTEM. On one occasion, however, a transition region from parent to product phase was observed in a stress gradient around a microcrack in the thin foil<sup>12</sup>. Here it was found that the correlation lengths as well as the amount of shear of those ISD's favoured by the actual stress component increased at the expense of domains distorted along other variants. At the same time the wavelength of the micro-modulation shuffle in the distorted parent phase decreased to about 1.0 nm, before the entire lattice was transformed into martensite and stacked with the ( $\bar{5}2$ ) sequence. Recent NMR studies by Rubini, Dimitropoulos, Aldrovandi, Borsa, Torgeson & Ziolo were also interpreted in terms of a continuous formation of martensite with an incomplete degree of deformation<sup>13</sup>, again confirming the above picture. An increasing degree of distortion when approaching the transition temperature was also observed in bulk thermal expansion experiments by Liu, Finlayson, Smith & Tanner<sup>14</sup>.

The same samples as used for the HRTEM imaging have also been extensively studied by inelastic neutron scattering. As indicated above, some precursor phenomena can be recognised by the behaviour of a given phonon branch or dispersion curve. As in most other B2 austenite crystals the  $TA_2[110]$  phonon branch is very low, corresponding with a low  $C'$  shear modulus, i.e. the ability for the  $(110)[\bar{1}\bar{1}0]$  shear, and reflecting the high anisotropy of this material. When approaching the transformation temperature the energy of the entire branch decreases further together with a softening of  $C'$ . In figure 3a some measurements of this branch in 62.5 at.% Ni (i.e. the case with 14M martensite) and at different temperatures approaching the martensitic transformation from above are shown<sup>15</sup>. The most apparent feature is clearly the dip in the dispersion curve at  $q = 1/6 [110]$  which implies an extra softening of the transverse displacement phonon of this wave-vector. At other compositions this dip fades away corresponding with the loss of the micro-modulation as in figure 2b and the step towards simply twinned  $L1_0$  as martensite instead of a well-defined ( $\bar{5}2$ ) stacking. Although the dip deepens upon cooling it never reaches zero in the austenite, i.e. there is no complete softening, indicating the first order character of the martensitic transformation. Figure 3b shows the same branch but now under external stress<sup>16</sup>. Here it is seen that the dip shifts to shorter wavelengths with increasing load. Although the present phonon data correspond with dynamical phenomena, the similarity between the wave-vector at the dip and that of the static micro-modulation of figure 2a is apparent. Also the change of wavelength with increasing stress can be related with the reported structural changes in the stress gradient<sup>12</sup>.

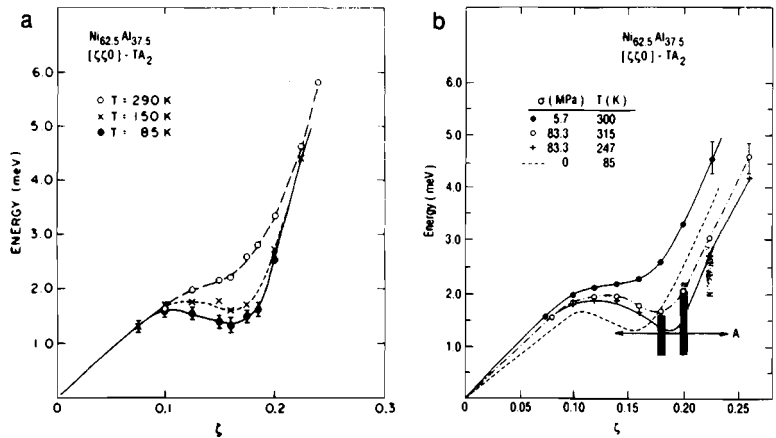


Figure 3: Phonon dispersion curves obtained by inelastic neutron scattering revealing precursor behaviour prior to the 14M transformation in Ni-Al. The dip at  $q = 1/6 [110]$  (a) deepens upon cooling<sup>15</sup> and (b) shifts under an external load<sup>16</sup>.

Similar phenomena were recently observed in Ni-Mn based ternary alloys. For the binary alloys, changing the composition results in different stacking sequences with relatively large unit cells<sup>10</sup>. As a result, possible precursing micro-modulations would be difficult to see inside the small ISD's. Also, in these alloys  $M_s$  is far above room temperature inhibiting atomic resolution. However, when alloying Ni<sub>50</sub>Mn<sub>50</sub> with Ti or Al by replacing Ni or Mn or both with the alloying element shorter stacking sequences are found in the fct martensite<sup>17</sup>. Again the transition temperature strongly depends on the composition and in the case of Ni<sub>43.8</sub>Mn<sub>42.4</sub>Ti<sub>13.8</sub> the transition occurs around room temperature and the austenite phase can be observed close to  $M_s$ . In this particular case the martensite has a  $(2\bar{2})$  sequence which implies a  $(110)[1\bar{1}0]$  shuffle modulation with a wavelength of 4 planes. As for Ni-Al the reciprocal space of the austenite reveals the same type of diffuse intensity, now with a satellite at  $1/5 [110]$ . When observing this precursor situation under HRTEM conditions in an  $[001]$  zone again ISD's with micro-modulations can be recognised<sup>18</sup>.

This is shown in figure 4 together with a blow-up of the satellites around a  $\bar{1}10$  reflection and a schematic for the interpretation of the HRTEM contrast. From the image it is clearly seen that within each ISD every other  $\{110\}$  plane is highlighted. Depending on the actual location the white dots in these planes are smeared out (A) or shifted parallel to the chosen plane (B). Both pictures can be explained by assuming a  $(110)[1\bar{1}0]$  transverse displacement wave with a periodicity of 4  $(110)$  planes and with an amplitude decreasing when moving away from the centre of the ISD<sup>11</sup>. The position of the satellite in reciprocal space at  $1/5$  instead of  $1/4$  can be explained by noting that the correlation lengths of the micro-modulations are rather small which leads to a lot of out-of-phase mismatches between two adjacent ISD's. As a result the diffraction satellite which stems from an overview including a large number of ISD's as well as mismatches will be averaged between the actual periodicity inside each ISD and the boundary features between two ISD's. So far these HRTEM images are the only microscopical evidence of precursor phenomena in this material.

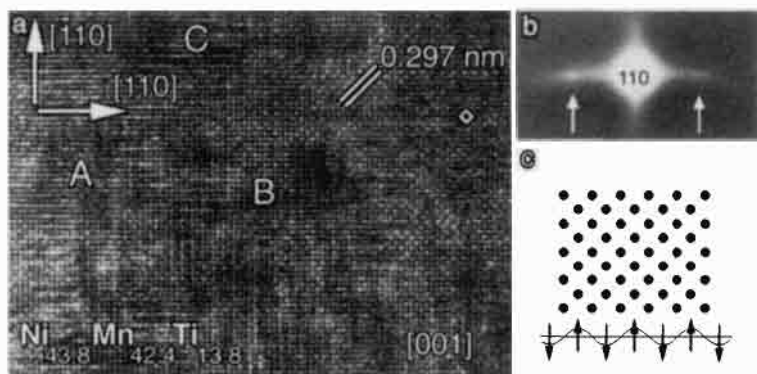


Figure 4: (a)  $[001]$  HRTEM image of the austenite with static precursor distortions observed prior to the  $(2\bar{2})$  sequence in Ni<sub>43.8</sub>Mn<sub>42.4</sub>Ti<sub>13.8</sub>. (b) corresponding satellites around a  $\bar{1}10$  reflection and (c) schematic of the transverse displacement wave<sup>18</sup>.

When the distorted austenite as shown in figure 4 is observed for a prolonged time under 400 keV electron irradiation the transformation towards the martensitic structure is started. This is shown in figure 5 where the situation after 1 and 5 minutes is seen<sup>18</sup>. First the amplitude of the transverse distortions increases yielding clear microtwin stackings inside some ISD's. At the same time the correlation length of the modulation increases especially in the direction of the wave-vector. At a later stage the correlation also increases in the direction

perpendicular to the wave-vector and a plate-like organisation between different martensite variants becomes apparent. The line in figure 5b shows the average location of a martensite-martensite interface parallel with a former (010)<sub>bcc</sub> plane, in accordance with regular martensite plates in this material. A similar nucleation of martensite plates was observed earlier in the previous material, Ni<sub>62.5</sub>Al<sub>37.5</sub> yielding the expected 7 layer periodicity<sup>19</sup>.

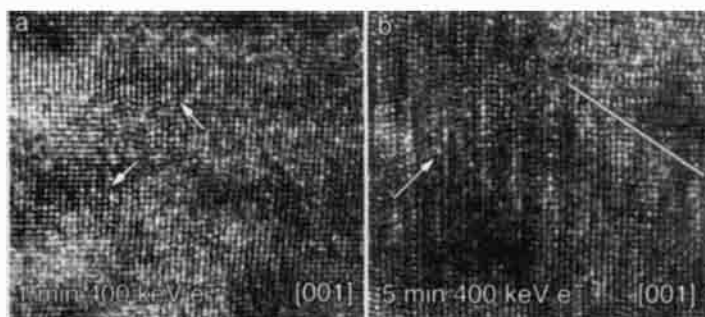


Figure 5: (a) [001] HRTEM image of the distorted austenite of figure 4 after (a) 1 min. and (b) 5 min. irradiation with 400 keV electrons inside the microscope<sup>18</sup>. The increase of the modulation amplitude is apparent. The line in (b) indicates an interface between two adjacent martensite variants.

A third system which displays very similar phenomena is that of the ternary alloy Ni<sub>2</sub>MnGa which has an L<sub>21</sub> Heusler structure in the parent phase. Again the martensitic phase transformation corresponds with a distortion towards a bct lattice plus an extra transverse modulation of one family of (110) planes. Here a periodicity of 5 planes was measured<sup>20</sup>. Above the transition temperature several precursor features similar in nature to those described above for the Ni-Al and Ni-Mn-Ti systems are again recognised. In figure 6 an [001] HRTEM image revealing a severely perturbed square pattern which indeed reflects a configuration of ISD's in the ideal bcc lattice<sup>21</sup>. The size of the domains is roughly 4 to 6 nm and alternating light/dark bands of appr. 1.2 nm parallel with the {110} planes are observed within the domains. As in the previous examples this modulated contrast is explained by (110)[110] transverse displacement waves now with a periodicity of about 6 (110) planes. These static distortions give rise to the expected satellites at 1/6 [110] in elastic scattering experiments, as seen from the intensities plotted from neutron<sup>21</sup> and x-ray diffraction<sup>22,23</sup> experiments in figure 7a and b, resp.. The acoustic TA<sub>2</sub> [110] branch again shows a clear dip at the same wavelength which softens but without reaching zero when approaching M<sub>s</sub><sup>21</sup>.

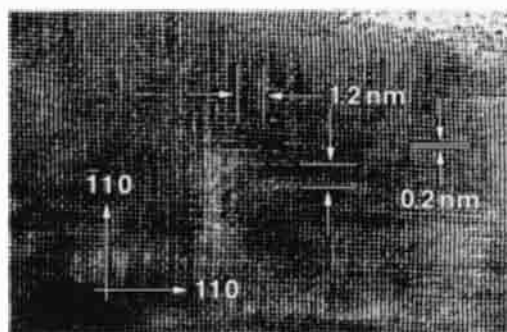


Figure 6: [001] HRTEM image of the distorted austenite of L<sub>21</sub> Ni<sub>2</sub>MnGa Heusler alloy clearly revealing modulated ISD's. The modulation wavelength is appr. 6 (110) planes (courtesy Zheludev et al.<sup>21</sup>).

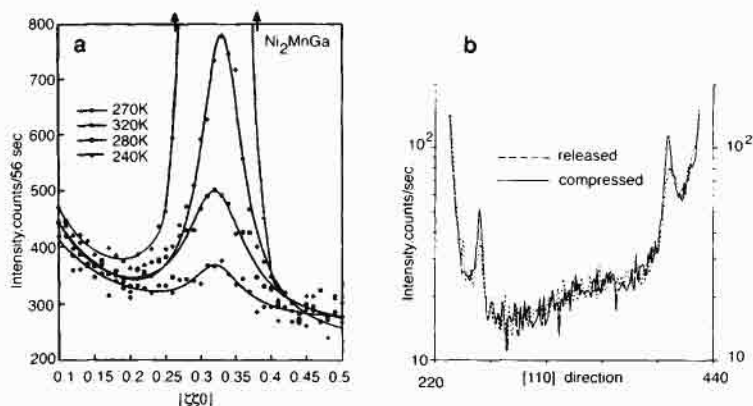


Figure 7: Intensity lines from (a) neutron (temperature dependent, courtesy Zheludev et al.<sup>21</sup>) and (b) x-ray elastic scattering experiments (stress dependent, courtesy Martynov et al.<sup>22,23</sup>) showing the existence of a satellite at  $1/6 [110]$  corresponding with the modulation wavelength in the ISD's visible in figure 6.

Although the above results again point towards a relation between the precursing distortions and the martensite shuffles, detailed analysis of the neutron scattering data in the temperature region close to  $M_s$  indicate that an intermediate phase may exist with an effective 6-layer periodicity<sup>21</sup>. In this view the ISD modulations could rather be precursors to this intermediate phase than to the final martensite structure.

Another interesting situation exists in the ternary  $\text{Ti}_{50}\text{Pd}_{50-x}\text{Cr}_x$  alloys which again have a B2 ordered parent phase. For the binary  $\text{TiPd}$  compound the martensite has an hexagonal close packed stacking yielding a B19 structure. When the ternary alloying content is increased  $M_s$  decreases and at  $x = 7$  a new and incommensurately modulated phase, again formed using the typical  $(110)[\bar{1}\bar{1}0]$  shears, is observed at room temperature<sup>24</sup>. In contrast to the above shown micro-modulations inside the ISD's the present modulation has a much larger correlation length, as seen from the HRTEM image in figure 8. The modulations can be described by a sinusoidal wave with wave-vector  $\mathbf{q} = 0.31 [110]_{\text{bcc}}$ . As a result of the lowered symmetry, the microstructure consists of twin related plates. At higher temperatures this material reveals the typical tweed contrast characteristic of two-beam images of B2 materials. The internal atomic distortions underlying this tweed remain unknown.

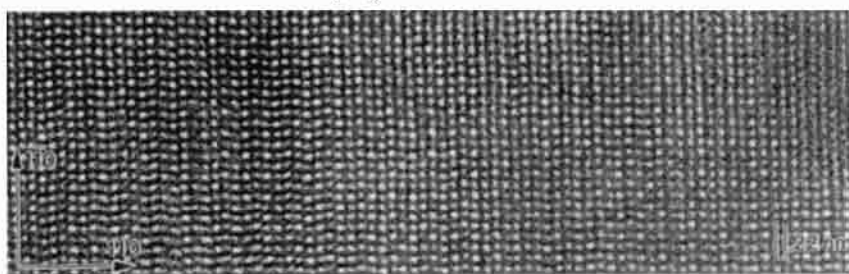


Figure 8: HRTEM image of the incommensurately modulated phase observed at room temperature in  $\text{Ti}_{50}\text{Pd}_{43}\text{Cr}_7$ . The modulations can be described by a sinusoidal wave with wave-vector  $0.31 [110]_{\text{bcc}}$  (courtesy Schwartz et al.<sup>24</sup>)

For this particular system, the phonon branches are not investigated as yet but, based on the accumulated knowledge on other B2 materials transforming to close packed structures, one would expect a low lying  $[110]$   $\text{TA}_2$  branch in the B2 range, possibly with a dip at  $1/2$

which would relate to the direct formation of the hexagonal stacking in the binary alloy. However, the appearance of the modulated phase with a clearly different periodicity would suggest a dip around  $1/3$  for the ternary system with 7 at.% Cr.

Many other bcc based systems, mainly Cu or Au binary or ternary alloys, also exhibit a martensitic transformation towards a close packed structure. Irrespective of the actual ordering the  $[110]$  transverse acoustic phonon branches are extremely low and will in many cases reveal a dip at  $2/3$   $[110]$ . An extended review of neutron scattering studies on these and other alloys was recently published by Nagasawa & Morii<sup>1</sup>. In some cases, the final martensite stacking will indeed be produced by a  $2/3$  wave, e.g. 9R or 18R (6M<sup>7</sup>). In other cases, however (sometimes even in the same alloy but with a different composition), the martensite structure is of the 2H (2O<sup>7</sup>) type which cannot be related to the  $2/3$  dip. In some of these cases elastic scattering reveals satellites in the  $\langle 110 \rangle$  diffuse intensity rods again at the  $2/3$  positions. Unfortunately, until now no HRTEM images have been obtained of examples in which the phonon dip does not correspond with the martensite stacking. This is partially due to the fact that the corresponding modulation wavelength is too short for proper imaging, certainly at temperatures different from room temperature.

## Other Systems

Among other systems transforming martensitically from a bcc-based parent phase are those which result in a more complex structure such as in the case of NiTi and AuCd. Again inelastic neutron scattering studies have shown pronounced effects on the transverse  $[110]$  branch including a dip at or close to  $1/3$ <sup>1,25</sup>. Although the exact atomic configurations of the product phases are still unknown the similarity in behaviour with the more extensively studied systems above leads to the conclusion that also in these cases a relation with the ensuing transformation is expected.

Some of the above discussed precursor phenomena are also observed prior to diffusion driven phase transformations. A typical example are the conventional EM tweed images obtained in the tetragonal parent phase in high  $T_c$  superconductors<sup>26</sup> and other ceramics. In a recent survey by Putnis & S $\ddot{e}$ ne of such observations it was concluded that in these cases the tweed contrast resulted from underlying microstructures formed by symmetry changes driven by cation ordering<sup>27</sup>. These symmetry changes yield a fine patchwork of twin related domains which coarsen when the transformation proceeds. However, in view of the diffusion driven character of the latter examples, these cases should be clearly separated from those in the field of the martensites.

## DISCUSSION AND CONCLUSIONS

From the examples shown above it is seen that more and more precursor situations are documented by direct atomic resolution images revealing the actual static lattice distortions existing in the parent phase before it transforms to the martensite. This has especially been the case for those transformations which involve a relatively large shuffle wavelength of several (4-7)  $(110)_{\text{bcc}}$  planes and of which the precursors can be observed at room temperature. The two cases which have also been investigated by inelastic scattering (Ni-Al and Ni<sub>2</sub>MnGa) reveal a dip in the  $[110]$  TA<sub>2</sub> phonon branch at a wave-vector very close to that corresponding with these static distortions.

In a general concept of a symmetry-restricted anharmonic theory Krumhansl relates the phonon anomalies to the electron band topology<sup>28</sup>. The latter is directly determined by the competition of nearest neighbour interactions which in turn can be a function of stress, composition and temperature<sup>1,29</sup>. Nagasawa, Yoshida & Makita simulated the  $\langle 110 \rangle^*$

transverse acoustic mode in  $\beta$  phase alloys on the basis of interplanar force constants<sup>1</sup>; the competition between these effective forces indeed yields a phonon anomaly or dip. They also show that these interaction parameters are affected by localised stress fields of proper symmetry in such a way that the dip deepens with increasing stress. In a detailed study of the parent phase anomalies in the Heusler  $\text{AuCuZn}_2$  alloy Nagasawa and co-workers concluded that at least part of the observed phenomena (again a  $2/3$  dip in the  $[110]$  branch) could be attributed to the arrangements of vacancies in the high temperature phases<sup>30</sup>. In limiting the contributions to second and third nearest neighbour interactions one obtains dips at or near  $2/3 \langle 110 \rangle^*$ ; it can, however, be expected that an increase in the number of interaction parameters could yield dips at more esoteric locations such as the  $1/6$  in Ni-Al.

According to Krumhansl the dispersion anomalies together with the strong anisotropy of the  $\beta$  phase will naturally, i.e., through the anharmonic terms, produce "static embryo-like regions of internally modulated correlated structures"<sup>31</sup>, where the wave-vector of the modulation is given by the position of the dip in the phonon dispersion curve. Gooding & Krumhansl applied this theory to the Ni-Al bcc - 14M transformation<sup>32</sup>; in the latter case they were indeed able to describe the 14M structure as a superposition of a homogeneous shear ( $q = 0$ ) and a modulated distortion ( $q \neq 0$ ) based on the coupling of the anisotropy and the phonon anomaly, which agrees well with the observed micro-modulations. In principle this coupling can exist without any pre-existing defects. However, the stress field produced by a local defect can in turn couple with the transformation strain. Even the weakest lattice perturbation (e.g., arising from differences in the atomic sizes of the alloy constituents<sup>5,1</sup>), if it has the proper transformation-related symmetry, will couple with the softened static response. Although Krumhansl indicates that close to  $M_s$  (in the order of a few degrees above) an intrinsic periodically modulated strain pattern can be obtained without the existence of physical defects, a "real" parent lattice, as-quenched from solution treatment, will provide a wide spectrum of preferred sites for the local stabilisation of static strain patterns. The most numerous defect sites arise from the effects of atomic size differences, impurities, point defects, ordering errors, etc. and are usually of relatively low strain amplitude. Robertson & Wayman<sup>5</sup> suggested that a unique source for local tetragonal distortions in Ni-rich Ni-Al would be the atomic size difference effect associated with the excess nickel atoms randomly distributed on aluminium sublattice sites. As shown by Becquart, Clapp & Rifkin using molecular dynamics, heterogeneous defects such as the compositional disorder of excess Ni atoms on the Al sublattice could indeed induce the observed small distortions<sup>33</sup>. These then contribute to the evolution of the microstructure observed as tweed or micro-modulations, but are seen as too weak to become potent nucleation sites. On the other hand, the remaining lattice defects, which are far fewer in number (e.g., dislocations, dislocation tangles, grain boundaries as well as the microcracks), have significantly higher associated strain fields and thus, in case of proper symmetry, a greater nucleation potential as the temperature approaches  $M_s$ . More recently the ISD model was included in the anharmonic approach and thus considered as a static response of the lattice to its interatomic interactions<sup>34</sup>. Further support for these ideas has come from first-principles calculations by Zhao & Harmon yielding the proper phonon anomalies which are attributed to the nesting of the Fermi-surface<sup>35</sup>.

The above presented and referred experimental data together with the extensive theoretical models existing today provide ample material for a detailed understanding of the actual atomic structures and their anomalous behaviour in the different precursor states. These descriptions, however, do not immediately imply that these phenomena have a direct influence on the ensuing transformation or the final atomic structure of the product phase. Indeed, the fact that some alloys show  $2/3 [110]$  dips while transforming into a hexagonal instead of cubic stacking already indicates that in these cases the characteristics of the shuffles in the martensite structure will be determined by other forces. Even for Ni-Al, where the correlation between the precursor micro-modulation and the final martensite stacking is apparent, it was



shown by Khatchaturyan, Shapiro and Semenovskaya<sup>36</sup> that the 14M structure can be regarded as a so-called adaptive phase in which the actual lattice parameters and stacking are compatible with the linear geometrical theory describing the crystallographic features of a martensitic transformation, solely based on the lattice distortions and concept of minimal stress at the parent-product interface<sup>37</sup>. On the other hand, the existence of large shuffle amplitudes in some precursor states or other intermediate configurations as well as the evolution during irradiation<sup>18,19</sup>, i.e. without a clear-cut interface, towards actual martensite stackings indicate that the parent phase characteristics alone can also influence or even dictate the final structure<sup>38</sup>. In order to delineate the relative contributions of the different forces playing a role in the determination of the actual martensite structure more investigations have to be performed especially in the field of energy calculations in the austenite and metastable martensite phases. A first principles exercise in this direction, although dealing more with ordering reactions, was performed by Sluiter, Turchi, Pinski & Stocks for Ni-Al and Ni-Ti<sup>39</sup>.

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## PRE-TRANSFORMATION LATTICE STRAIN ANISOTROPY AND 'CENTRAL PEAK' SCATTERING

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### INTRODUCTION

Displacive lattice transformations, which are characterised by a diffusionless shear process have been extensively studied by metallurgists and physicists. In the language of the former these are referred to as martensitic, for the latter 'soft-mode'.

'Soft mode' refers to a mode of lattice vibration with the eigenvector corresponding to the static atomic displacements which result in the transformed phase and for which the frequency,  $\omega \rightarrow 0$  as the temperature is lowered towards the transformation temperature,  $T_M$ . The softening may take place at the zone centre, in which case there is a decrease in the corresponding elastic modulus, or at a wave vector close to a reciprocal space lattice vector for the new phase. The origin of the soft-mode behaviour is well understood in terms of the renormalization of the mode frequencies due to anharmonic effects.<sup>1</sup> A less well understood feature of the 'soft-mode' transition is the development of an elastic component in the phonon scattering, the so-called 'central peak', which diverges as  $T_M$  is approached. Two theoretical approaches have been proposed; one dynamical and linked with the anharmonic behaviour,<sup>2</sup> the other arising from the static distortion of the lattice due to defect-induced strain fields.<sup>3</sup>

The term 'martensite' originated as the name given to the transformation product obtained from quenching particular ferrous alloys, but the usage has become broadened to cover a wide variety of shear-based transformations, including those associated with 'soft-mode' behaviour. This has led to some degree of confusion as the traditional martensitic transformations from a face-centred cubic to a body-centred tetragonal structure involve a large volume change (thermodynamically a first-order transition), whereas the 'soft-mode' transition is continuous in volume (a second-order transition).

A distinguishing feature of the soft-mode martensitic transformation is the anomalous pre-transformation behaviour that is observed in a range of physical and microstructural

properties at temperatures well above  $T_M$ .<sup>4</sup> These so-called ‘precursors’ are assumed to occur because of the microstructural modulation that occurs in the parent phase above  $T_M$ .

High-resolution dilatometric measurements have revealed the appearance of anisotropy in the cubic-phase thermal strain in the precursive temperature region for the soft-mode martensitic transformations in  $V_3Si$ ,<sup>5</sup>  $Ni-Al$ ,<sup>6</sup>  $In-Tl$ ,<sup>7</sup> and  $SrTiO_3$ .<sup>8</sup> In the case of  $Ni-Al$ <sup>9</sup> and  $SrTiO_3$ ,<sup>10</sup> the onset temperatures for the strain anisotropy are close to those at which the appearance of ‘central peak’ behaviour occurs.

It is the purpose of this paper to review briefly the thermal strain anisotropy data and to consider the implications for the ‘central peak’ scattering.

### EXPERIMENTAL DETAILS

A characteristic precursive phenomenon is the development of martensite transformation bands as a stress-relieving mechanism resulting in twinning in the product phase. For the systems considered here the transformation is associated with shears on  $\{110\}_c$ . Thus, in the simplest case, the  $\{110\}_c$  twin-separation plane may have any one of six possible orientations, though in practice, crystal imperfections will introduce an energy difference, which will favour a particular orientation and which may vary across the crystal. Thus, the transformation phase of a cubic, single-crystal parent is expected to be composed of a number of misaligned domains. It is therefore necessary to control the morphology of the transformed crystal such that the measuring direction for the thermal dilatometry is a single crystallographic direction for the entire crystal.<sup>7</sup> In the case of the  $\langle 100 \rangle$  measurements considered here, control was exercised by the application of an external stress, either uniaxial ( $\sim 5 \times 10^4$  Pa) along the direction of measurement,  $l$ , or biaxial ( $\sim 30$ – $160 \times 10^4$  Pa) along the two  $\langle 100 \rangle$  axes perpendicular to  $l$ . These stresses are too small to produce any detectable change in  $T_M$ .

The thermal strain measurements were made in a low-temperature, high-resolution, three-terminal, capacitance dilatometer identical to the design of White and Collins.<sup>11</sup>

### REVIEW OF PRECURSIVE THERMAL STRAIN ANISOTROPY

#### Indium-Thallium Alloys

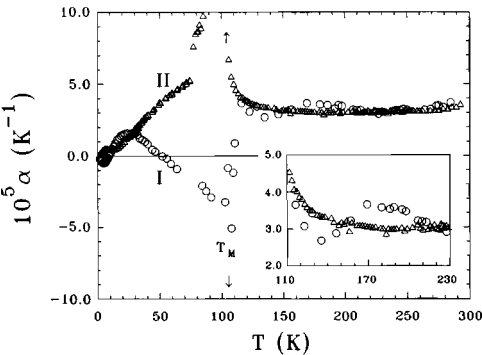


**Figure 1.** Thermal-expansion coefficients measured on cooling (300–77K and 4.2–2K) and heating (4.2–77K) along  $\langle 001 \rangle_c$  directions for  $In-26.5$  at% $Tl$  in the temperature range 2–300K, with different external stress fields applied. (From reference 7)

A martensitic, cubic-to-tetragonal transformation occurs with  $T_M$  varying from 425K to near 0K for indium-thallium, solid-solution alloys in the composition range 15.5 to 31 at% $Tl$ . The ‘soft-mode’ character of the transition is seen in the vanishing of the shear modulus,  $c' [= \frac{1}{2} (c_{11} - c_{12})]$ ,<sup>12</sup> although ‘central peak’ scattering has not been reported.<sup>13</sup> The  $c'$  shear modulus is associated with the  $\{110\}\langle 110 \rangle$  phonon mode. However, careful neutron inelastic scattering measurements of phonon groups at low  $\zeta$  along the  $[\zeta\zeta 0][\zeta\zeta 0]$  branch as a function of temperature in the cubic state for  $In-Tl$  single crystals, failed to reveal any softening of phonon frequencies.<sup>14</sup> On the contrary, the frequencies at the lowest

resolvable  $\zeta$  appeared to increase with decreasing temperature.

The precursive anisotropy in the thermal expansion for an In-26.5at%Tl alloy is shown in Figure 1 taken from reference 7, where for curve I the measurement direction becomes a “c” axis in the transformed crystal and for curve II it becomes an “a” axis.

### V<sub>3</sub>Si

The A15 structure compound V<sub>3</sub>Si undergoes a soft-mode, martensitic, cubic-tetragonal transformation at  $T_M \approx 21\text{K}$ , as evidenced by  $c' \rightarrow 0$ .<sup>16</sup> Although ‘central peak’ scattering has not been observed for V<sub>3</sub>Si, it has been well documented for the  $[\zeta\zeta 0][\zeta\zeta 0]$  phonon branch of the related A15 compound Nb<sub>3</sub>Sn<sup>2</sup> ( $T_M \approx 40\text{K}$ ). There is an extensive history of dilatometric studies of single-crystal and polycrystalline V<sub>3</sub>Si<sup>5,17</sup> that have revealed precursive thermal strain anisotropy. Precursive thermal strain anisotropy has also been observed for polycrystalline Nb<sub>3</sub>Sn.<sup>18</sup> The temperature dependence of the thermal strain for single-crystal V<sub>3</sub>Si with externally controlled morphology is reproduced from reference 5 in Figure 2. The extent of precursive thermal strain anisotropy can be seen from Figure 3 where the temperature dependence of the crystal distortion derived from the data in Figure 2 is reproduced. Note also the comparison with the considerably smaller crystal distortion in In-26.5at%Tl.

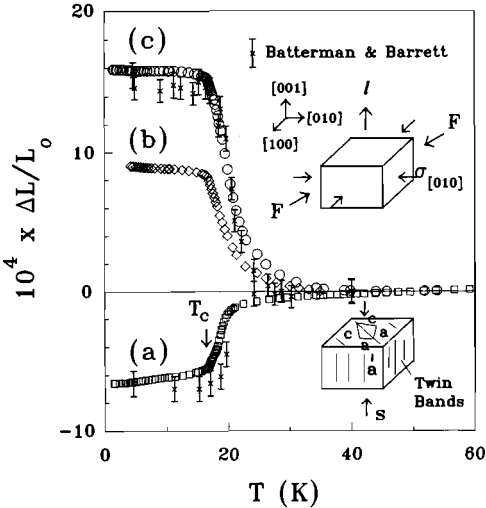


**Figure 2.** Thermal strain vs temperature curves for V<sub>3</sub>Si measured along [001] on heating (4.2–60K) and cooling (4.2–1.5K). Curve (a) is for an uniaxial stress ( $s \approx 0.03\sigma_{(100)}$ ) along [001]; (b) and (c) are for biaxial stress applied along [100] and [010] with  $0.5\sigma_{(100)}$  and  $\sigma_{(100)}$ , respectively. The x-ray data of Batterman and Barrett (reference 15) are also plotted for comparison. The insets show the directions of applied stresses and [in case of the curve (a)] the martensite-phase domains. (From reference 5)

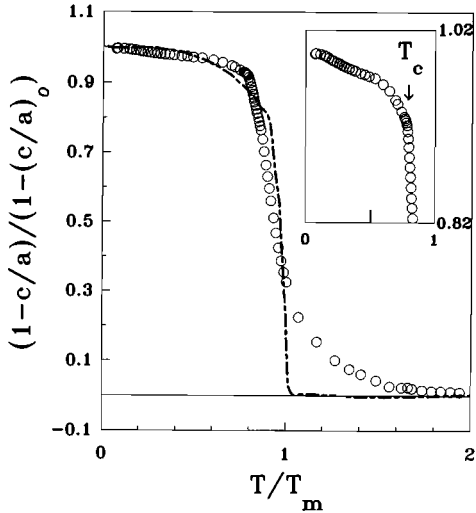


**Figure 3.** The temperature dependence of the crystal distortion for V<sub>3</sub>Si, (o), derived from the data in Figure 2 [curves (a) and (c)], as discussed in reference 5. The dot-dashed curve shows the same distortion parameter for In-26.5 at%Tl derived from the data in Figure 1. The inset shows in detail the data below the superconducting critical temperature,  $T_c$ . (From reference 5)

### Nickel-Aluminium Alloys

A martensitic transformation from a cubic CsCl-type structure by  $\{110\}\{1\bar{1}0\}$  type shears occurs for Ni<sub>x</sub>Al<sub>1-x</sub> alloys in the composition range  $0.615 < x < 0.64$ .<sup>19</sup> Precursive

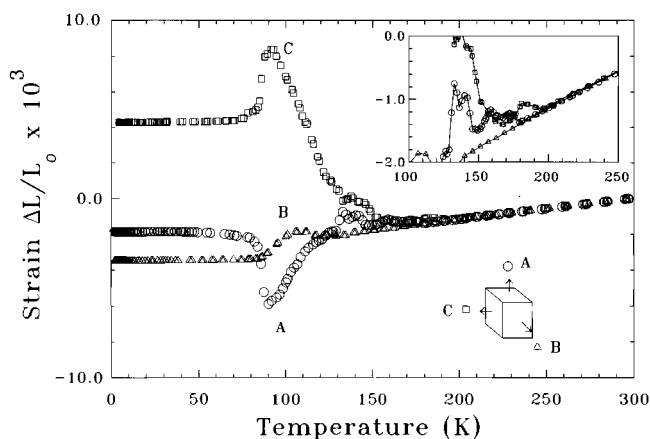


**Figure 4.** Thermal strain for a single-crystal  $\text{Ni}_{0.625}\text{Al}_{0.375}$  alloy measured on cooling along three  $\langle 100 \rangle_c$  directions in a capacitance dilatometer. The inset shows in detail the data in the temperature range 100-250K. (From reference 6)

softening of a transverse  $[\zeta\zeta 0][\bar{\zeta}\bar{\zeta} 0]$  phonon mode is again associated with the transformation, but in contrast to the In-Tl alloys and A15 compounds, the softening occurs away from the zone centre and the 'central peak' scattering develops at the same wave vector.<sup>9</sup>

The temperature dependence of thermal strain for a single crystal of  $\text{Ni}_{0.625}\text{Al}_{0.375}$  reproduced from reference 6 in Figure 4 represents the richest display of precursive anisotropy so-far observed. The anomalous 'wiggling' in the A and C directions that occurs between 200 and 130K has been unambiguously identified with surface tilting associated with the formation of martensite bands. This is then followed by the smooth, distinctly tri-axial-like anisotropic expansion that continues with reducing temperature to  $T_M$ . It has been argued<sup>6</sup> that this expansion behaviour is indicative of the pre-transformation development of the orthorhombic transformation phase. Unfortunately, it was not possible to control the morphology of the transformation phase by the application of external stress.

## Strontium Titanate

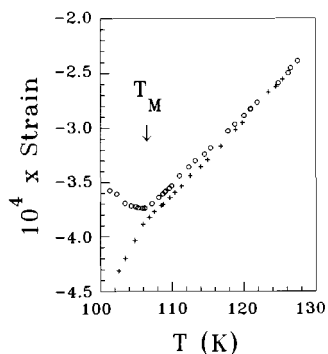


**Figure 5.** Thermal strain for  $\text{SrTiO}_3$  heated along cubic  $[001]$  under different stress conditions.

$\text{SrTiO}_3$  represents a different case. While the cubic-to-tetragonal structural transformation at 105K has never been described as martensitic, it is nevertheless a soft-mode displacive transition exhibiting characteristic 'martensite bands' associated with twinning on  $\{110\}$ .<sup>20</sup> It also displays 'central mode' scattering associated with the zone-boundary softening of the rotational mode of vibration of the  $\text{TiO}_3$  octahedra. As yet unpublished<sup>8</sup> dilatometric measurements of thermal strain for a single crystal of  $\text{SrTiO}_3$  in the vicinity of  $T_M \approx 105\text{K}$  are presented in Figure 5. Under different stress conditions  $[001]$  becomes either the tetragonal "a" or "c" axis below  $T_M$ . The departure from an isotropic thermal strain at  $\sim 120\text{K}$  is evident.

## DISCUSSION

The thermal strain measurements described above have the common feature of anisotropic behaviour in a supposed isotropic state (cubic structure). These observations go well beyond the short-range, static strain fields associated with the lattice impurities responsible for Huang scattering. This then raises the question of the temperature at which the lattice symmetry changes and the implications of this for the 'central mode' scattering.

Both of the current models for the 'central mode' scattering contain the implicit assumption of cubic symmetry above  $T_M$ . Possibly because of the dramatic nature of the soft-mode behaviour and a ready understanding of the structural transformation in terms of it, there was a strong incentive to establish a link between it and the 'central mode' scattering. A consistent difficulty with this approach is the failure to establish an intrinsic line-width for the 'central mode' peak and the unspecified nature of the mechanism responsible for a low-frequency resonance in the energy of the soft mode.<sup>21</sup>

While there is evidence<sup>22</sup> in support of a lattice impurity or defect-induced, strain-field mechanism, this model has not enjoyed wide support.

The observation of the departure from cubic symmetry above  $T_M$  co-incident with the appearance of the 'central peak' scattering serves to resolve the conflict between dynamic and lattice strain models. The departure from cubic symmetry may be attributed to a shift in the atomic equilibrium position associated with the soft-mode anharmonicity. In such a picture, the 'central peak' then becomes the precursor to a Bragg reflection for the new structure.

There is already strong evidence to support this argument. Riste et al.<sup>10</sup> noted for  $\text{SrTiO}_3$  that for the central peak 'its neutron intensity varies from superlattice point to superlattice point as the Bragg intensity below  $T_c$  does' (here  $T_c \equiv T_M$ ). In the case of cubic (CsCl-type)  $\text{Ni}_{0.625}\text{Al}_{0.375}$ , Shapiro et al.<sup>9</sup> report the development of elastic central peaks close to the wave vector for which softening occurs in the  $[\zeta\zeta 0]$  transverse acoustic mode. These peaks lie close to Bragg peaks in the pseudo-rhombohedral transformation phase. It has also been reported<sup>23</sup> for  $\text{Ni}_2\text{MnGa}$  that 'Strong temperature-dependent elastic scattering was observed at wave vectors close to  $\zeta_0$ , which develops into a Bragg peak of an intermediate phase as the martensitic transition temperature is approached'.

Such off-zone-centre, soft-mode systems offer the most favourable conditions for a test of the hypothesis that the 'central peak' is a precursor to a Bragg reflection in the transformation phase. Zone-centre softening, such as occurs in  $\text{Nb}_3\text{Sn}$ ,<sup>2</sup> results in the 'central mode' scattering emerging from an existing Bragg peak, which ultimately splits in the lower symmetry transformation structure, which presents a problem with resolution.

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# CALCULATING GRAIN BOUNDARY ENERGIES AND OTHER DEFECT ENERGIES IN ORDERED ALLOYS

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## INTRODUCTION

The calculation of the excess free energy of a grain boundary, a surface or a dislocation core in a material requires: (a) calculation of the free energy of a large region containing the defect, and (b) subtraction of the sum of the chemical potentials of each of the atoms within the region. The result in an ordered alloy depends critically on exactly how one draws the boundary in (a), and a thermodynamically consistent procedure will be described for doing this. The chemical potentials depend sensitively on the stoichiometry of the alloy; the slope of chemical potential versus composition at the stoichiometric composition becomes infinite as  $T \rightarrow 0\text{K}$ . It is shown for a binary alloy how the chemical potentials can be obtained analytically within a dilute solution approximation, based on calculations of the three basic point defect energies.

The aim is to give a general approach which can be followed when total energies are calculated by both semi-empirical and ab initio methods.

The situation is envisaged in which the total energy of a box of atoms can be calculated, and one wants to obtain the excess energy of an interface which has been constructed within the box. The simplest situation is if a static calculation has been made and the atomic positions are relaxed to the structure of minimum energy. However, free energy calculations are also feasible. Periodic boundary conditions parallel to the interface are employed, and perhaps also three dimensional periodicity, which implies that two boundaries per box are necessary. These technicalities as well as the method for calculating energies will not be discussed further here.

The basic formula for the excess free energy of an interface is [1]:

$$\Gamma \cdot A = E_{\text{box}} - \sum_i n_i \mu_i \quad (1)$$

where



- $\Gamma$  = excess free energy of interface  
 $A$  = area of the piece of interface included in the box  
 $E_{\text{box}}$  = total calculated energy inside the box drawn around the interface. This should be the Gibbs free energy. An approximation to it would be the internal energy at  $T=0\text{K}$ .  
 $n_i$  = number of atoms of species  $i$  within the box  
 $\mu_i$  = chemical potential of species  $i$ .

We refer to the planes which close the box parallel to the boundary as the *terminating* planes. Between the terminating planes, the box includes one or more translational unit cells of the system parallel to the boundary. We therefore have to assume that the system is periodic parallel to the boundary, but this assumption is anyway necessary for practical schemes of calculation. The terminating planes should be far enough away from the interface to be locally in the undistorted bulk material.

Whereas much work has been done on improving the theory and technology for calculating total energies and atomic positions in large systems, this paper addresses two difficulties which have received less attention. The first is how we obtain the chemical potentials. These quantities are sensitively dependent on the deviation from stoichiometry and the concentrations of point defects, so the calculation of point defect concentrations is addressed first. In cases where the dominant defects are antisite defects rather than vacancies, chemical potentials have been calculated as a function of stoichiometry by Monte-Carlo simulation, including "transmutation" of atomic species [2-5]. A chemical potential difference is postulated and the system is equilibrated to obtain the corresponding stoichiometry. This is an effective method, but besides its computational cost it suffers from two disadvantages. Firstly, the possible contribution of vacancies is not taken into account and secondly no insight is obtained into the physical meaning of the chemical potentials or their dependence on the parameters of the models.

The second difficulty is where to locate the terminating planes. In the case of an ordered alloy the microscopic position of these planes with respect to the unit cell might make a difference to the result, and it has to be correctly chosen, as discussed in detail below.

## POINT DEFECTS IN BINARY ORDERED ALLOYS

We consider an AB alloy which consists of an equal number of A and B sites. For the subsequent analysis, every site is uniquely associated with either an A or a B sublattice. The following is trivially generalised to  $A_mB_n$  alloys. The alloy is not quite stoichiometric, and has the composition  $A_xB_{1-x}$ , where for the validity of the independent defect approximation we must suppose  $x$  to be within a few percent of 0.5. Each site of each sublattice can be occupied by its own atom, an atom of the other kind (an antisite defect) or a vacancy. There are therefore six species for which we define the concentrations on each sublattice:

- $c_{aa}$  = concentration of A atoms on the A sublattice  
 $c_{bb}$  = concentration of B atoms on the B sublattice  
 $c_{ab}$  = concentration of A atoms on the B sublattice  
 $c_{ba}$  = concentration of B atoms on the A sublattice  
 $c_{va}$  = concentration of vacancies on the A sublattice  
 $c_{vb}$  = concentration of vacancies on the B sublattice

These are the six unknowns in a statistical model of the concentrations. They satisfy the following three constraints:

The sum rules for concentrations:

$$\begin{aligned}c_{aa} + c_{ba} + c_{va} &= 1 \\c_{bb} + c_{ab} + c_{vb} &= 1\end{aligned}\quad (2)$$

The given ratio of A and B atoms:

$$(1-x)(c_{aa} + c_{ab}) = x(c_{bb} + c_{ba}). \quad (3)$$

Since there are six unknowns and three equations, there are three independent variables. We can associate these with any three elementary independent modes of point defect formation which conserve the numbers of atoms. These are like basis vectors for representing arbitrary point defect concentrations. Let us define them as follows:

I. Double vacancy: an atom from an A site and an atom from a B site occupy two new sites, leaving two vacancies behind. Denote the energy required by  $e_{2v}$ .

II. Triple defect on A: two atoms vacate B sites and occupy new A and B sites, thus creating two B vacancies and an A antisite defect. Denote the energy required by  $e_{ta}$ .

III. Triple defect on B: two atoms vacate A sites and occupy new A and B sites, thus creating two A vacancies and a B antisite defect. Denote the energy required by  $e_{tb}$ .

Any other modes we can think of are a linear combination of these. For example the double antisite, which is formed by exchanging a pair of A and B atoms, is equivalent to  $II + III - 2 \cdot I$ . This would be an equally good choice as a "basis vector" instead of one of the three above.

## Point Defect Energies

The practical definition of single point defect energies in ordered alloys has been a source of some confusion. For an element, the procedure is clear. In order to calculate the vacancy formation energy for example, one first calculates the energy of a block of  $N$  atoms containing a vacancy and then subtracts from it the energy of  $N$  atoms in a perfect crystal. The  $N$  atoms provide a reference system, for which there is more than one strategy to obtain the energy. The important point is that the same number of atoms are compared, with and without the defect. But what is the reference system for an ordered alloy?

If all we want at the end of the calculation are the equilibrium point defect concentrations, we do not need single point defect energies but rather the multiple defect energies, the energies of the vacancy pair and the triple defects defined above. It should be emphasised that the members of these multiple defects are assumed not to be physically associated. The possibility of defect clustering is not addressed here. Such a multiple defect can be introduced into a crystal without changing its stoichiometry. It is therefore possible to compare the energy of a block of  $N$  atoms containing a pair of vacancies or a triple defect with the energy of the same number of atoms in a perfect crystal. In practice however, the above multiple defect energies can be constructed simply from calculations of individual point defect energies, although these calculations involve an arbitrary choice of reference system. One can be sure, however, that when the point defect energies are combined to give the above physically meaningful multiple defect energies, the arbitrariness in their individual values will cancel.

A useful way to approach these individual point defect energies is to define the energy per mole or cohesive energy of perfect material with respect to separated free atoms,  $e_{mol}$ . We can then arbitrarily divide this between the atoms of type A and B so that:

$$e_{mol} = e_{aa} + e_{bb} \quad (4)$$

where the subscript  $aa$  denotes an atom of type A on a site of type A. If we use classical descriptions of the total energy, such as pair potentials or embedded atom potentials, there is a natural allocation of the energy to individual atoms. It is not a unique division of the energy between A and B, because an arbitrary energy could be added to  $e_{aa}$  and subtracted from  $e_{bb}$  without changing any physical consequences. The choice of free atoms to define a

reference energy for each element is also arbitrary. An alternative convention, usual in chemistry, would be to refer to the elements in their standard states, but this is less convenient for atomistic calculations. The energy  $E$  of a block containing  $N$  sites of sublattice A and  $N$  sites of sublattice B is now written as:

$$E = N(c_{aa}e_{aa} + c_{bb}e_{bb} + c_{ab}e_{ab} + c_{ba}e_{ba} + c_{va}e_{va} + c_{vb}e_{vb}), \quad (5)$$

where the point defects are assumed to be sufficiently dilute that interactions between them may be neglected. This formula prescribes how to calculate the individual point defect energies. Firstly a block is constructed containing, say,  $N$  sites of type A fully occupied by atoms of type A, and  $N-1$  sites of type B occupied by atoms of type B and a vacancy or antisite on the remaining site of the B sublattice. Denoting the total energy of this block by  $E$ , the point defect energy is given by:

$$e_{\text{defect},b} = E - Ne_{aa} - (N-1)e_{bb}. \quad (6)$$

In terms of the point defect energies so defined, our stoichiometry-conserving defects have formation energies given by:

$$\begin{aligned} e_{2v} &= e_{va} + e_{vb} \\ e_{ta} &= 2e_{vb} + e_{ba} - e_{bb} \\ e_{tb} &= 2e_{va} + e_{ab} - e_{aa}. \end{aligned} \quad (7)$$

Notice that this approach is not restricted to any particular method of total energy calculation or any assumption that the energy is localised on an atomic site, so it is suitable for ab initio calculations. Furthermore, this formalism is generalised to finite temperature  $T$  if for *energy* we read *free energy*, in which case the point defect free energies should include their  $T$  dependence and vibrational entropy. Finally, if the pressure  $p$  is not zero we should add  $p\Omega_i$  to each of the energies in (5), where the  $\Omega_i$  are the six corresponding partial volumes. Like the energy, the volume can be divided arbitrarily between perfect a and b sites.

## Point Defect Concentrations

From the law of mass action it is straightforward to show that the concentrations satisfy the following three equations:

$$\begin{aligned} c_{va}c_{vb} &= \exp(-\beta e_{2v}) \\ c_{va}^2c_{ab}/c_{aa} &= \exp(-\beta e_{tb}) \\ c_{vb}^2c_{ba}/c_{bb} &= \exp(-\beta e_{ta}) \end{aligned} \quad (8)$$

where  $1/\beta$  is Boltzmann's constant times temperature.

At  $T=0K$ , the criterion of minimum energy dictates that only one defect, the constitutional defect, is present. In NiAl for example this is the Ni antisite ( $c_{ab}$ ) in Ni-rich alloys, and the Ni vacancy ( $c_{va}$ ) in Al-rich alloys [6]. The constitutional defects will be the dominant ones at high temperatures. The criterion that the A antisite should be the constitutional defect in A-rich alloys is:

$$e_{tb} < 2e_{2v}, \quad (9)$$

otherwise the B vacancy is the constitutional defect. Similarly the criterion that the A vacancy be the constitutional defect in B-rich alloys is:

$$e_{ta} > 2e_{2v}, \quad (10)$$

otherwise the B antisite is the constitutional defect. These inequalities should be satisfied for example by models of NiAl.

By eliminating the concentrations in turn from eqns.(2), (6) and (8), we obtain a quartic equation which is most simply obtained numerically. However, we can obtain good approximate solutions in limiting cases. Firstly, we can set the  $c_{aa}$  and  $c_{bb}$  equal to unity to a

good approximation if the total concentration of point defects is reasonably small. Now consider the case of Ni-rich NiAl. Let the concentration of constitutional Ni antisites be  $c_{ab}^0 = 2x - 1$ . There is a thermal concentration of Ni-antisites we can denote by  $\Delta c_{ab}$  such that:

$$c_{ab} = c_{ab}^0 + \Delta c_{ab}. \quad (11)$$

If we now suppose we are in a regime where the constitutional antisites dominate the thermally excited ones, which will usually be the case if the excess of Ni is more than a percent or so, or if the temperature is low, then after some algebra we obtain the following solution:

$$c_{va} = \frac{\exp(-\beta e_{tb}/2)}{\sqrt{c_{ab}^0}} \quad (12)$$

$$c_{vb} = \sqrt{c_{ab}^0} \exp[-\beta(e_{2v} - e_{tb}/2)] \quad (13)$$

$$c_{ba} = \frac{\exp[-\beta(e_{ta} + e_{tb} - 2e_{2v})]}{c_{ab}^0} \quad (14)$$

$$c_{ab} = (2x - 1) + c_{ba} + (1 - x)c_{va} - xc_{vb} \quad (15)$$

which is only valid as long as all the concentrations are  $\ll 1$ .

On the other side of stoichiometry, we know from experiment that the constitutional defect in NiAl is the vacancy, so we can assume that  $c_{va}$  dominates the defect populations. In this case we obtain the solution:

$$c_{ab} = \frac{\exp(-\beta e_{tb})}{(c_{va}^0)^2} \quad (16)$$

$$c_{vb} = \frac{\exp(-\beta e_{2v})}{c_{va}^0} \quad (17)$$

$$c_{ba} = (c_{va}^0)^2 \exp[-\beta(e_{ta} - 2e_{2v})] \quad (18)$$

$$c_{va} = \frac{1 - 2x}{1 - x} + \frac{c_{ab} - c_{ba} + xc_{vb}}{1 - x}. \quad (19)$$

The constitutional vacancy concentration in this case is given by

$$c_{va}^0 = (1 - 2x)/(1 - x). \quad (20)$$

Very close to the stoichiometric composition, where the thermal defects dominate the constitutional defects, the results are more complicated.

Several points are worth noting about these formulae. Firstly, the concentrations follow an Arrhenius law except for the constitutional defect, however in no case is the activation energy a single point defect formation energy. Secondly, in a quantitative calculation the activation energy should include a temperature dependence of the formation energies and their formation entropies. The latter will appear as a preexponential factor, for example, the first equation becomes

$$c_{va} = \frac{\exp(s_{tb}/2k_B) \exp(-\beta e_{tb}/2)}{\sqrt{c_{ab}^0}}. \quad (21)$$

Finally, the total preexponential factor includes the stoichiometry deviation represented by  $c_{ab}^0$  or  $c_{va}^0$  so an extrapolated Arrhenius plot will show an intercept which is very sensitive to composition. Experimental data will be hard to reproduce both because of stoichiometry variations and because of the slow approach to thermal equilibrium.

## CHEMICAL POTENTIALS

Unlike the energy of an atom, which can be defined in terms of its local atomic environment, its chemical potential is a truly non-local quantity. In thermal equilibrium the chemical potential of each species is a constant throughout the system, whether atoms are at the interface or in the bulk.

For example, consider a system which is a stoichiometric ordered oxide at 0K at ambient pressure. If we make the system deviate from stoichiometry by the addition of a single oxygen atom, which goes into an interstitial site, the chemical potential of oxygen in the system is now the change in free energy when a second extra oxygen atom is added, call it  $\mu+$ . Likewise, if we make the system deviate from stoichiometry by removing just one oxygen atom, the new chemical potential of oxygen in the system is again the change in its free energy when one oxygen is added, restoring stoichiometry, call it  $\mu-$ . At low temperature, the difference between  $\mu+$  and  $\mu-$  is enormous, because in the sub-stoichiometric system the added oxygen is very happy to fill the vacancy in order to bring the system into equilibrium, whereas in the super-stoichiometric system it is forced to form a second interstitial. Thus the chemical potential of oxygen is a discontinuous function of composition at the stoichiometric composition. At finite T the discontinuity in chemical potential as a function of composition will be smeared out to some extent, but there will still be a rapid variation of chemical potential over a relatively small range of composition. From the local point of view, the environment of any oxygen atom is not affected; it only feels the presence of the defect in a statistical sense when a time average is taken. If we pick any oxygen atom in the lattice, its environment is infinitesimally different whether one atom of oxygen more or less is present in the system, yet its chemical potential is significantly affected by that one atom! That is why chemical potentials are much harder to calculate than total energies. This rapid variation in chemical potential has been measured in the case of the chemical potential of Al in FeAl and NiAl [7,8]. It should be clear from this discussion that in a general binary alloy, the T=0K limiting values of the chemical potentials depend on the nature of the constitutional defect. They have been tabulated in [9].

At finite temperature the chemical potentials can be calculated as follows. In the dilute solution approximation, the Gibbs free energy is given by:

$$G = N \sum_i (c_i e_i + c_i k_B T \ln c_i). \quad (22)$$

The subscript i labels the six concentrations and energies defined previously. It is straightforward to show that by minimising G with respect to the  $c_i$ , subject to the three constraints, we recover the three equations for the  $c_i$  predicted by the law of mass action.

By differentiating G with respect to  $N_a$ , the number of atoms of type A, we obtain the chemical potential  $\mu_a$ . In doing so care must be taken to include the dependence of N on the number of atoms via the equation:

$$N_a = N(c_{aa} + c_{ab}). \quad (23)$$

More simply, the chemical potentials appear as Legendre multipliers when G is minimised, associated with the constraints on total numbers of atoms, eg. (23). The results are:

$$\mu_a = e_{aa} - e_{va} + kT \log(c_{aa}/c_{va}) \quad (24)$$

and similarly:

$$\mu_b = e_{bb} - e_{vb} + kT \log(c_{bb}/c_{vb}). \quad (25)$$

Equivalent formulae can be produced in terms of the other point defect concentrations by substituting from (8).

The chemical potentials have been evaluated numerically by Hagen using embedded atom models for the defect energies [10]. An important finding was that good quantitative

agreement with Monte-Carlo calculations at 1000K could only be obtained when the full temperature dependence of the  $e_i$  was included.

Having discussed how, at least in principle, the chemical potentials can be calculated, I now turn to the second conceptual difficulty in implementing eqn.(1).

## TERMINATION OF THE BOX

The question of how to terminate the box is fundamental to all the calculations of interfacial energy in compounds, including the calculation of surface energies. It has been addressed previously for particular cases by Chetty and Martin [11,12]. These authors pointed out that a suitable termination is one which is on a symmetry plane of the crystal, or which follows symmetry planes if it is not parallel to the boundary. However, it may not always be possible to find a symmetry plane. I offer a solution here which is more general. It reconciles the atomistic picture with the thermodynamic limit.

Let us consider the choice of terminating plane normal to the x-axis, such that the material to the left of it will be counted in the box and the material to the right (the side on which x is greater) will be counted as outside the box. Now in the thermodynamic description one does not deal with individual atoms but with statistical averages. In this spirit we have to consider the average of the excess quantity over an ensemble, each member of which has the plane in a random position. In fact it need not be a plane at all but a surface which meanders along approximately parallel to the interface. On the macroscopic scale, on which thermodynamic quantities are defined and the atomic granularity is invisible, this surface appears planar. The result for the excess quantity to the left of such a meandering surface will be the same as if we average over an ensemble of planes in random x-positions.

For practical calculation it will often prove possible to define a *representative termination* in such a way that it gives the same excess as the ensemble average.

For a plane located at x the excess energy with respect to the material to the left of x is

$$\Gamma_{\text{ex}}(x) = \Gamma_{\text{ex}}(0) + \frac{1}{A} \int_0^x (e(x') - \mu(x')) dx' \quad (26)$$

For convenience, the local energy and chemical potential have been written as continuous functions of x, it being understood that

$$e(x) - \mu(x) = \sum_i (e_i - \mu_i) \delta(x - x_i) \quad (27)$$

where the summation is over all atoms within the area of the unit cell A parallel to the interface. The origin of x is in the undistorted bulk material, far from the boundary, but otherwise arbitrary.

The integral in eqn.(26) is periodic in x, with period L, the length of the unit cell parallel to x. This is because although e and  $\mu$  are not equal for individual atoms in the unit cell, their sums over the unit cell are equal, so that:

$$\int_0^L (e(x) - \mu(x)) dx = 0 \quad (28)$$

wherever the origin of x; provided of course that this unit cell is far from any interfaces or defects. It is therefore only necessary to take the ensemble average of eqn.(26) within a single unit cell. The ensemble average is therefore

$$\bar{\Gamma}_{\text{ex}} = \Gamma_{\text{ex}}(0) + \frac{1}{AL} \int_0^L dx \int_0^x (e(x') - \mu(x')) dx' \quad (29)$$

which on integrating by parts becomes

$$\bar{\Gamma}_{\text{ex}} = \Gamma_{\text{ex}}(0) + \frac{1}{A} \int_0^L (1 - x/L)(e(x) - \mu(x)) dx. \quad (30)$$

This gives us the following recipe for constructing an appropriate termination. With some arbitrary origin  $x=0$ , we should include in the box all atoms with  $x < 0$ . In addition, to reproduce the integral in eqn.(30) we should include atoms in the range  $0 < x < L$  weighted by the fraction  $(1-x/L)$ . I refer to this as a *tapered termination*. From the tapered termination we could construct a *representative* termination if there are equivalent atoms at different heights  $x$  of the unit cell. We can do this by rearranging all the fractions of atoms onto equivalent sites so as to make the termination as *sharp* as possible. A representative termination may for some crystal structures be a sharp termination, ie a termination which corresponds to a simple planar truncation.

In practice it is only necessary to do the total energy calculation for the block with some convenient termination at the origin of  $x$  and to calculate the excess energy  $\Gamma_{\text{ex}}(0)$  for this case. The true excess energy can then be obtained by adding the excess energy of the correct terminating piece. An example should make the procedure clear.

### Example: An AB alloy

For many cubic AB alloys such as NiAl or TiC, a termination in the (100) orientation presents the problem of alternating A and B planes. This simple example illustrates the procedure which can be applied easily to more complicated crystals and orientations. If we calculate the excess free energy by terminating outside an A plane we get a different answer to if we terminate outside a B plane, because  $e_A - \mu_A$  and  $e_B - \mu_B$  are not zero. Now let us apply the tapered termination. First choose the origin infinitesimally outside an A plane. Eqn.(30) tells us to include just the next B plane at  $x > 0$ , weighted by 1/2. In this case the representative termination is the same as the tapered termination; we should include just half of the physical terminating plane. It does not matter which element this is, A or B. Because only half the last plane is included, the termination is not sharp. It is as if we had a sharp termination running exactly through a plane of atoms, which is a mirror plane, and including just half of them.

An alternative choice of origin would be midway between A and B planes. Let us say that the first plane at  $x > 0$  is then a B plane. It must be weighted with 3/4. The following A plane has the weight 1/4. That completes the termination, which this time is truly tapered. The excess energy of a stoichiometric unit in the perfect crystal is zero. Thus the excess energy of  $3B/4 + A/4$  is equal to the excess energy of  $B/2$ , which was our first choice of termination.

In this case the result is rather trivial, but for more complex structures involving several atoms per unit cell the method is easily applied and the result may not be so obvious.

## CONCLUSIONS

Two problems in the calculation of interfacial energies in crystals have been addressed, namely how to obtain the chemical potentials and how to define the terminating planes on the atomic scale for the purposes of calculating the excess free energy.

Formula for the chemical potentials have been derived in terms of the formation energy of the four point defects. In the process the conceptual basis for calculating point defect energies in ordered alloys and the dependence of point defect concentrations on them has been clarified. The statistical physics of point defects in ordered alloys has been well described before [13], but the present work represents a generalisation in the sense that it is not dependent on any particular model, such as the Bragg-Williams approach with nearest neighbour bond energies. It is hoped that the results will be of use to theoreticians as well as

for the interpretation of experimental results. Further developments are envisaged to include the effects of defect clustering. This may be important in unravelling experimental data, in which a further complication is how closely thermodynamic equilibrium has been achieved.

Approximate formulae for the point defect concentrations close (but not too close) to the stoichiometric composition in AB alloys have been derived. They show that the prefactors in the Arrhenius formulae are sensitive functions of the stoichiometry, besides representing the usual formation entropy term.

To reconcile the atomic granularity with the thermodynamic definition of excess energy a procedure has been derived for defining the termination of a region containing the interface. This involves augmenting an arbitrarily chosen *sharp* terminating plane by a *tapered* termination, obtained by adding weighted contributions from the atoms within a single unit cell measured from the sharp termination. The weights are simply  $(1-x/L)$ , where  $x$  is the distance of the atom beyond the initial sharp termination and  $L$  is the width of the unit cell in the  $x$  direction.

Applications to the calculation of static grain boundary energies have been described elsewhere [9,10,14].

Exactly the same procedure can be followed to define the free energy of a dislocation core. It should be surrounded by a box, the terminating planes of which can be dealt with exactly as above. Special attention has to be given to the atoms at the corners of the box, but this presents no particular problems; their weights are simply a product of the weights generated by the planar terminations which they share.

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# ATOMISTIC STUDY OF STRUCTURE AND MOBILITY OF DISLOCATIONS IN NiAl

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## INTRODUCTION

The intermetallic alloy NiAl is discussed as a potential base alloy for high temperature structural materials. Its use is currently limited by low room temperature ductility and fracture toughness. Consequently, substantial research efforts have been directed towards understanding its mechanical behaviour [1, 2] so that detailed experimental [3, 4, 5] and theoretical [6, 7, 8] analyses of the deformation of NiAl are available today.

At room temperature, NiAl deforms almost exclusively by  $\langle 100 \rangle$  dislocations [4, 9, 10] and the availability of only 3 independent slip systems is thought to be responsible for the limited ductility of polycrystalline NiAl. Only when single crystals are compressed along the  $\langle 100 \rangle$  direction ('hard' orientation), secondary  $\langle 111 \rangle$  dislocations can be activated [3, 5]. Their mobility appears to be limited by the screw orientation [5] and yield stresses as high as 2 GPa are reported below 50 K [5]. However,  $\langle 110 \rangle$  dislocations are responsible for the increased plasticity in hard oriented crystals above 600 K [3, 7]. The competition between  $\langle 111 \rangle$  and  $\langle 110 \rangle$  dislocations as secondary slip systems therefore appears to be one of the key issues to explain the observed deformation behaviour of NiAl.

Since some earlier work based on anisotropic elasticity theory had not been successful in describing the observed mechanical behaviour of NiAl (for an overview see [11]), several studies have addressed dislocation processes on the atomic length scale [6, 7, 8]. Their findings are encouraging for the use of atomistic methods, since they could explain several of the experimental observations. Nevertheless, most of the quantitative data they obtained are somewhat suspicious. For example, the Peierls stresses of the  $\langle 100 \rangle$  and  $\langle 111 \rangle$  dislocations are rather similar [6] and far too low to explain the measured yield stresses in hard oriented crystals.

The objective of this work is to conduct molecular statics calculations of the core structure and the Peierls stresses of various dislocations in NiAl, using a recently developed embedded

atom (EAM) potential [12], specifically fit to the properties of B2 NiAl. The simulations are compared in detail to experimental results and, since atomistic modelling may be sensitive to details of the interatomic interaction, to previous atomistic studies.

## MODELLING TECHNIQUES

Dislocations are introduced into the centre of a cylindrical atomistic region by applying the displacement fields according to the anisotropic elastic solution for a Volterra dislocation [13] to all atoms in the cylinder. Periodic boundary conditions of minimal length are applied along the dislocation line. Atoms in the outermost shell (thickness larger than twice the cut-off radius of the potential) are kept fixed at the positions corresponding to the elastic solution, while all the inner atoms are relaxed using a conjugate gradient algorithm. Size scaling tests showed that a radius of the cylinder of about 10nm is sufficient to guarantee that the dislocation core is not influenced by the fixed boundary conditions. The differential displacement method [14] is used to display the relaxed dislocation cores. The Burgers vector distribution as defined in Ref. [15] allows the determination of the dislocation core width  $w$  (the distance between  $1/4$  and  $3/4$   $b$ ).

The effect of “driving” shear stresses on the dislocations are studied by superimposing a corresponding homogeneous shear strain on the whole model before relaxation. By repeating these calculations with increasing shear strains, the Peierls barrier is determined from the superimposed strain at which the dislocation starts moving.

The interatomic interaction is described by an EAM potential specifically developed for NiAl in the B2 structure [12]. Compared to the older potential [16], which was used in most of the previous atomistic studies, our new potential gives considerably higher antiphase boundary (APB) energies ( $\gamma_{APB}^{110} = 0.82 \text{ J/m}^2$ ,  $\gamma_{APB}^{211} = 1.06 \text{ J/m}^2$ ; in good agreement with the APB energies calculated from ab-initio methods [17]) and correctly reproduces the constitutional point defects for off-stoichiometric composition [12].

## RESULTS

The Burgers vectors, glide plane and line direction of the dislocations studied in this paper are given in table 1. Included in this table are also the results for the Peierls stresses as calculated here and, for comparison, those determined previously [6] with a different interatomic interaction model [16]. In the following we give for each of the three Burgers vectors under consideration a short description of the results.

$b = \langle 100 \rangle$ :

The core structure of the  $\langle 100 \rangle$  screw dislocation is planar and widely spread ( $w = 2.6b$ ) on the  $\{011\}$  plane. In consequence, the screw dislocation only moves on the  $\{011\}$  glide plane and does so at a low Peierls stress of about 60 MPa.

The edge dislocation on the  $\{011\}$  plane is again widely spread on the glide plane ( $w = 2.9b$ ) and moves with similar ease. In contrast, the edge dislocation on the  $\{001\}$  plane is more compact ( $w = 1.8b$ ) and significantly more difficult to move (see table 1). Mixed dislocations on the  $\{011\}$  plane have somewhat higher Peierls stresses than either edge or screw dislocations.

Although the results of the present study and of the above mentioned previous study [6] are qualitatively almost identical, the calculated values for the Peierls stresses differ quite significantly. We find that the highest Peierls stresses in the  $\langle 100 \rangle \{011\}$  glide system are as low as  $\approx 170 \text{ MPa}$ .

**Table 1:** Summary of the calculated properties of the various dislocations in NiAl. Dislocations are grouped together for different glide planes. The dislocation character, edge (E), screw (S) or mixed type (M) is indicated together with Burgers vector and line direction. The Peierls stresses for the  $\langle 111 \rangle$  dislocations on the  $\{211\}$  plane correspond to the asymmetry in twinning and antitwinning sense respectively.

| glide plane | Burgers vector        | line direct.          | cha-rac. | Peierls stress in GPa |              |
|-------------|-----------------------|-----------------------|----------|-----------------------|--------------|
|             |                       |                       |          | this work             | Rao-Pot. [6] |
| {100}       | $\langle 100 \rangle$ | 001                   | E        | \$ 1.08               | 2.58         |
|             |                       | 001                   | E        | & 0.88                | 2.58         |
|             |                       | 100                   | S        | >0.08                 | >0.27        |
|             |                       | 10 $\bar{1}$          | M        | 0.15                  | >6.0         |
|             | $\langle 110 \rangle$ | 1 $\bar{1}$ 0         | E        | \$ >6.0               | —            |
|             |                       | 110                   | S        | 1.85                  | —            |
|             |                       | 100                   | M        | 4.84                  | —            |
| {110}       | $\langle 100 \rangle$ | 011                   | E        |                       | 0.32         |
|             |                       | 100                   | S        |                       | 0.22         |
|             |                       | 1 $\bar{1}$ $\bar{1}$ | M        |                       | 1.16         |
|             |                       | 2 $\bar{1}$ 1         | M        |                       | —            |
|             | $\langle 110 \rangle$ | 001                   | E        | # >6.0                | >2.54        |
|             |                       | 110                   | S        | 4.2                   | >1.9         |
|             |                       | 11 $\bar{2}$          | M        | 4.2                   | —            |
|             | $\langle 111 \rangle$ | 2 $\bar{1}$ $\bar{1}$ | E        | ! 0.07                | 0.38         |
|             |                       | 111                   | S        | 2.0                   | 0.45         |
|             |                       | 100                   | M        | ! 0.23                | —            |
|             |                       | 011                   | M        | ! 0.06                | —            |
| {211}       | $\langle 111 \rangle$ | 1 $\bar{0}$ 1         | E        | ! 1.4 (3.0)           | 0.59         |
|             |                       | 111                   | S        | >3.5 (1.7)            | 0.74         |

\$ Ni-core, & Al-core, ! splitting, # decomposition

b =  $\langle 110 \rangle$ :

All the  $\langle 110 \rangle$  dislocations are very compact ( $w \approx 1.0b$ ) and very difficult to move. While the screw and the mixed dislocations can eventually be moved at rather high Peierls stresses (between 1.7 and 4.8 GPa), the edge dislocations are sessile up to stresses as high as 6 GPa. The  $\langle 110 \rangle \{1\bar{1}0\}$  then actually decompose into two  $\langle 100 \rangle$  dislocations. The very low mobility of the  $\langle 110 \rangle$  edge dislocations is probably due to atomic rearrangements in the dislocation core. An example for such rearrangements is shown in Figure 1, which displays the core configuration of the  $\langle 110 \rangle \{001\}$  edge dislocation with a Ni-core.

Comparing to the previous atomistic studies of  $\langle 110 \rangle$  dislocations in NiAl [7, 6], there are differences in many details but all studies clearly show that the edge dislocations are limiting the mobility.

b =  $\langle 111 \rangle$ :

In spite of the very high APB energy, most of the dislocations split into two  $1/2\langle 111 \rangle$  super-partials as shown in Figure 2. This is true for all dislocation characters studied, except for the pure screw dislocation which is displayed in Figure 3.

As a consequence edge and mixed  $\langle 111 \rangle$  dislocations move with relative ease, whereas the Peierls barrier for screw dislocations is as high as 2 GPa. These results are in contrast to previous calculations [6], which have shown a splitting for the screw dislocations and also a much lower Peierls barrier. However, our results can perfectly explain most of the experimental results concerning  $\langle 111 \rangle$  dislocations which will be discussed in the following section.

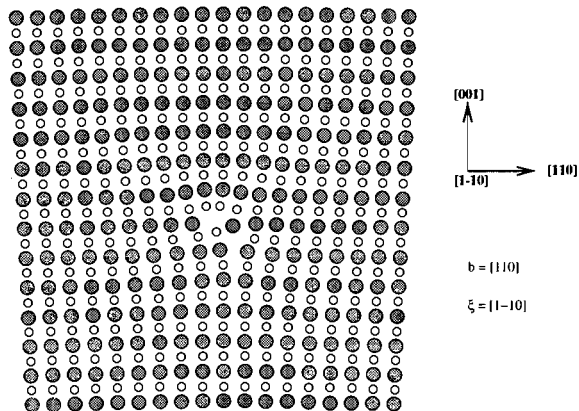


Figure 1: Core configuration of the  $\langle 110 \rangle \{001\}$  edge dislocation (Ni-core).

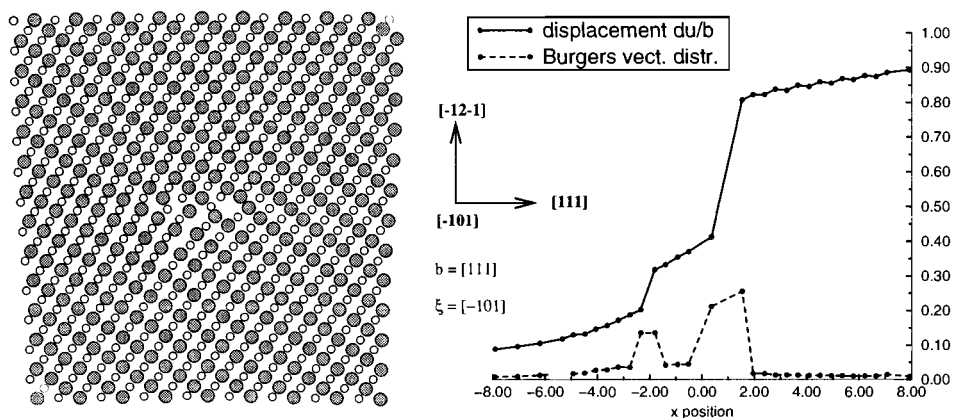


Figure 2: Core configuration and Burgers vector distribution of the  $\langle 111 \rangle \{211\}$  edge dislocation display separation into two superpartials.

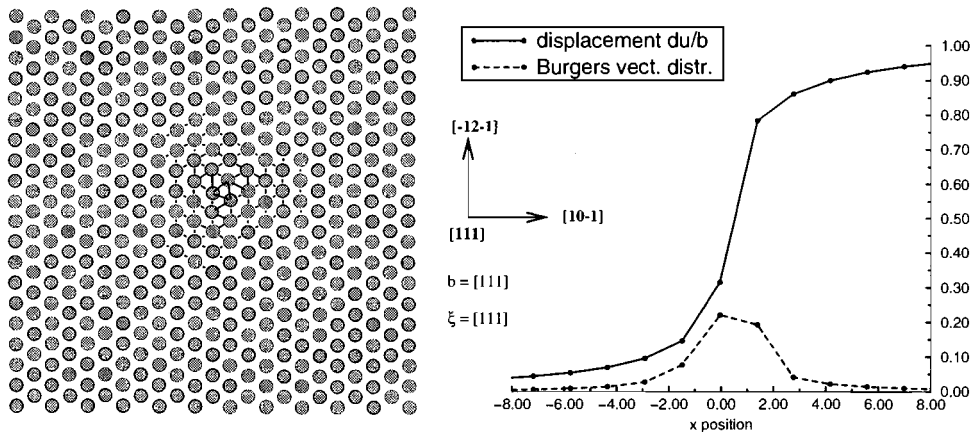


Figure 3: Core configuration of the  $\langle 111 \rangle$  screw dislocation. The Burgers vector distribution is calculated for a  $\{211\}$  cut and clearly shows a compact dislocation core.

## DISCUSSION

For the deformation of NiAl in a soft orientation our calculations give by far the lowest Peierls barriers for the  $\langle 100 \rangle \{011\}$  glide system. This glide system is also found in many experimental observations and generally accepted as the primary slip system in NiAl [18]. Compared to previous atomistic modelling [6], we obtain Peierls stresses which are markedly lower. The calculated Peierls stresses (see table 1) are in the range of 40-150 MPa which is clearly at the lower end of the experimental low temperature deformation data [18]. This may either be attributed to an insufficiency of the interaction model used here or one may speculate that the low temperature deformation of NiAl is not limited by the Peierls stresses but by the interaction of the dislocations with other obstacles (possibly point defects and impurities).

Deformation of NiAl in the hard  $\langle 100 \rangle$  orientation cannot be carried by the primary slip system but requires other Burgers vectors than  $\langle 100 \rangle$ . Our calculations, as well as the previous studies [6], suggest that the  $\langle 111 \rangle$  Burgers vector is the most favourable one for this orientation. However, while the previous studies gave Peierls stresses of the same order of magnitude as for the primary slip system, we find a much higher Peierls stress for the  $\langle 111 \rangle$  screw dislocation (c.f. table 1). The reason for this discrepancy has to be sought in the different core structure obtained for this dislocation. While our potential gives a rather compact core which is not separated into two superpartials (even under stress), other potentials always show such splitting.

Agreement with experimental observations is obtained in almost all details. Not only does the Peierls stress for the  $\langle 111 \rangle$  screw dislocations almost exactly reach the critical resolved shear stresses measured below 50 K [5], Transmission electron microscopy (TEM) observations reveal unequivocally long  $\langle 111 \rangle$  screw segments after deformation at these low temperatures [5]. This is a strong indication for a large difference in Peierls stresses for the screw and the other orientations of dislocation lines. Furthermore, these TEM observations show increasingly more frequent cross slip events from the  $\{110\}$  onto the  $\{211\}$  plane with decreasing temperature [5]. We can explain this with the somewhat lower Peierls stresses for the screw dislocations on the  $\{211\}$  plane (in the antitwinning sense) than on  $\{110\}$ .

The  $\{110\}$  dislocations are from our calculations not expected to contribute significantly to the plastic deformation in hard oriented NiAl because of the very high Peierls stresses. Experimentally, these dislocations do not appear unless the temperature is raised to about 600 K [18]. At this temperature the experimental data strongly suggest a transition from  $\langle 111 \rangle$  to  $\langle 110 \rangle$  slip.

This transition cannot be directly explained. However, we may rationalize this transition if we consider the factors limiting the operation of Frank-Read sources for these two types of dislocations. At low temperatures the  $\langle 110 \rangle$  sources are blocked due to the extremely high Peierls stress of edge dislocations, and the  $\langle 111 \rangle$  sources start to operate if a sufficiently high stress level is reached. As temperature increases, the Peierls barrier can eventually be overcome with the help of thermal activations and the line tension limits the operation of corresponding sources. Our calculations of the line energies, including dislocation core energies, result in a lower line tension for the  $\langle 110 \rangle$  than for the  $\langle 111 \rangle$  dislocations [19]. Consequently, at sufficiently high temperatures the activation of  $\langle 110 \rangle$  sources should overtake the  $\langle 111 \rangle$  sources.

## CONCLUSIONS

Dislocation core structures of  $\langle 100 \rangle$ ,  $\langle 110 \rangle$  and  $\langle 111 \rangle$  dislocations in NiAl have been studied by molecular statics calculations using a new many-body embedded atom potential. They

confirm that the  $\langle 100 \rangle \{011\}$  glide system is far easier to activate than any other slip system in NiAl.

Excellent agreement between experiment and our calculations is obtained when considering the low temperature deformation in the hard orientation. Not only are the Peierls stresses almost exactly as large as the experimental critical resolved shear stresses at low temperatures, but the limiting role of the screw character can also be explained. Furthermore the transition from  $\langle 111 \rangle$  to  $\langle 110 \rangle$  slip at higher temperatures can be understood when combining the present results with a simple line tension model.

## ACKNOWLEDGEMENTS

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## ATOMIC STRUCTURE AND PROPERTIES OF DISLOCATIONS AND INTERFACES IN TWO-PHASE TiAl COMPOUNDS

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### INTRODUCTION

Ordered intermetallic compounds have been investigated very intensively in the recent years since a variety of their properties make them superior in high temperature applications over the commonly used disordered alloys. Their elastic moduli are usually high and they have very high yield or fracture stresses that are maintained up to high temperatures. Moreover, compounds based on light elements, such as Ti and Al, can have very low densities and thus high strength-to-weight ratio. Furthermore, these alloys often have high melting temperatures and much lower self-diffusion coefficients than do disordered alloys and, therefore, higher creep strength and corrosion resistance. However, a very significant limitation is their much lower ductility and/or toughness at low temperatures than in disordered alloys (for recent symposia and reviews see Liu et al. 1995; Horton et al. 1995; Westbrook, and Fleischer 1995).

In between various intermetallics studied, TiAl is one of the most ductile alloys though still appreciably more brittle than pure metals or disordered alloys (for reviews see Yamaguchi and Inui 1993; Gnanamoorthy, et al. 1994). It crystallizes in  $L1_0$  tetragonal close-packed structure<sup>1</sup> and displays dramatically different microstructures for different compositions near the 50:50 Al:Ti ratio (McCullough, et al. 1988). The single-phase  $L1_0$  structure can only be produced in alloys with 52 at%Al, or more, and in practice  $L1_0$  TiAl single crystals are usually made with about 56 at % Al. Alloys containing less than 52 at % Al exhibit a two-phase microstructure composed of  $L1_0$  TiAl and a small volume fraction of

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<sup>1</sup> To a good approximation this structure can be regarded as f.c.c. based with (002) planes composed alternatively of Ti and Al; the cubic crystallographic notation is, therefore, commonly used. If we denote as  $c$  and  $a$  the lattice parameters in the [001] and [100]/[010] directions, respectively, the  $c/a$  ratio is 1.02 at the stoichiometric composition and increases to 1.03 at Al-rich compositions (Duwez and Taylor 1952; Huang, et al. 1987).

DO<sub>19</sub>/Ti<sub>3</sub>Al. These materials possess a lamellar structure consisting of layers of twin-related TiAl and layers of Ti<sub>3</sub>Al; in single crystalline form they are called "polysynthetically twinned (PST) crystals" (for a recent review see Yamaguchi, et al. 1995).

Deformation properties of single-phase and two-phase structures are remarkably different. At room temperature the main deformation mode in PST crystals is twinning on {111} planes along the  $\langle 112 \rangle$  direction. Slip by ordinary  $1/2\langle 110 \rangle$  dislocations on {111} planes is the complementary deformation mode while  $\langle 101 \rangle$  superdislocations are usually not observed at this temperature (Inui, et al. 1992a; Inui, et al. 1992c; Farenc, et al. 1993; Farenc and Couret 1993). At high temperatures twinning is still active, but its propensity decreases, and slip is accommodated by both ordinary dislocations and superdislocations. In contrast, single-phase aluminum rich TiAl deforms at room temperature by the glide of  $\langle 101 \rangle$  superdislocations. At high temperatures the slip is dominated by ordinary  $1/2\langle 110 \rangle$  dislocations while superdislocations are not observed but twinning becomes active at temperatures around 800°C; the latter is an unusual phenomenon since twinning is commonly a low temperature deformation mode. The single phase TiAl single crystals also exhibit a pronounced yield stress anomaly, i. e. increase of the yield stress with increasing temperature (Kawabata, et al. 1985; Yamaguchi, et al. 1995).

An interesting question is then whether this distinction arises due to the presence of interfaces in PST crystals or different compositions, in particular different content of aluminum. However, even if the latter is controlling, as suggested by some recent studies (Girshick and Vitek 1995; Mahapatra, et al. 1995), this does not explain the relatively high ductility and toughness obtainable in the two-phase lamellar TiAl and the strong dependence of the deformation behavior of PST crystals on the orientation of the compressive axis relative to the interfacial plane (Fujiwara, et al. 1990). The origin of these phenomena must be sought in the effect of interfaces and two alternatives need to be considered. First, if interfaces are to enhance the ductility they must serve as efficient sources of dislocations and/or twins. Secondly, since interfaces are natural obstacles to slip and twinning the corresponding transmission process must be relatively easy.

Considering the phenomena described above, it is unlikely that a fundamental understanding of the deformation behavior of TiAl can be achieved on the macroscopic and/or mesoscopic level. First, the choice of the slip system is principally controlled by the dislocation core spreading and/or possible dislocation dissociations which, in turn, depend on the existence of metastable stacking fault like defects (for reviews see Duesbery and Richardson 1991; Vitek 1992, 1996). Moreover, the dislocation core is the main factor controlling the lattice friction (Peierls) stress and this may be a very significant contribution to the yield stress, particularly in less symmetrical structures. Secondly, the interaction of dislocations and interfaces is very short ranged since interfaces are not associated with any long range elastic fields. Hence, both the dislocation core and interfacial phenomena need to be investigated on atomic level.

The precursor of such atomistic studies is a description of atomic interactions or, generally, knowledge of the dependence of the total energy of the system on the positions of the atoms. In principle, this is available in ab-initio total energy calculations based on the local density functional theory (see, for example, Pettifor and Cottrell 1992). However, for extended defects, such as dislocations and interfaces, such calculations are only feasible when the number of atoms included into the calculation is well below one hundred. Hence, only very special cases can be treated in this framework and, indeed, the bulk of the dislocation and interfacial



modeling has been made using much simpler approaches to the description of atomic interactions. In recent years the most successful were the embedded atom method (Daw and Baskes 1984) and many body potentials of the Finnis-Sinclair type (Finnis and Sinclair 1984).

In this paper we first present Finnis-Sinclair type potentials constructed for TiAl and summarize the results of a study of dislocation cores performed using these potentials (Girschick and Vitek 1995). However, in this scheme the atomic interactions are central, dependent only on the separation of atoms and, directional, covalent type character of bonding is neglected although such bonding is present in this compound, for example between the nearest neighbor Ti atoms (Fu and Yoo 1990; Woodward, et al. 1991). The importance of directional bonding is then demonstrated for an ordered twin boundary the structure of which was studied both by modeling and high resolution electron microscopy (HREM). The observed structure displays an asymmetry which is not reproduced when employing the central forces. In contrast, the ab-initio electronic structure calculations using the full-potential LMTO method (Methfessel 1988; Methfessel, et al. 1989) reveal an asymmetric structure which is in an excellent agreement with observations. Nevertheless, it is argued that when interpreted with care, the results of calculations employing central-force interactions can provide valuable insights. This is demonstrated by the analysis of the deformation behavior of TiAl in the light of the above mentioned studies of the dislocation cores.

## FINNIS-SINCLAIR TYPE POTENTIALS FOR TiAl

The Finnis-Sinclair type potentials (Finnis and Sinclair 1984) are central-force potentials but have a many-body character in that the energy of a system of particles is not merely a sum of pair interactions between individual atoms. In this scheme, modified for binary alloys by Ackland and Vitek (1990), the total energy of a system of N atoms is written as

$$E = \sum_{i=1}^N \left[ \frac{1}{2} \sum_{j \neq i} V_{S_i S_j}(r_{ij}) - \sqrt{\rho_{S_i}} \right] \quad (1a)$$

where

$$\rho_{S_i} = \sum_{j \neq i} \Phi_{S_i S_j}(r_{ij}) \quad (1b)$$

The suffices i and j refer to individual atoms and  $S_i$  and  $S_j$  to the species of the atoms involved. The summation over j extends over those neighbors of the atom i for which  $r_{ij}$ , the separation of atoms i and j, is within the cut-off radii of these potentials. The second term in Equation (1a) is the attractive many-body term and both V and  $\Phi$  are empirically fitted pair potentials. A justification for the square root form of the many-body function is provided in the framework of a second moment approximation of the density of states to the tight-binding theory incorporating local charge conservation; in this framework the potentials  $\Phi$  represent squares of the hopping integrals (Ackland, et al. 1988).

For the Ti-Al system the pair potentials  $V_{TiTi}$  and  $\Phi_{TiTi}$  are slightly modified potentials originally constructed for the pure Ti (Ackland 1992) and  $V_{AlAl}$  and  $\Phi_{AlAl}$  are potentials that have been used in studies of Ni-Al alloys (Vitek, et al. 1991). As suggested by Ackland and Vitek (1990)  $\Phi_{TiAl}$  is taken as

$$\Phi_{TiAl} = \sqrt{\Phi_{TiTi} \Phi_{AlAl}} \quad (2)$$

which is consistent with its interpretation in terms of the hopping integrals. The pair potential  $V_{TiAl}$  was constructed so as to reproduce for the  $L1_0$   $TiAl$  the cohesive energy, lattice parameters  $a$  and  $c$  and, approximately, the elastic moduli; the potentials then also closely reproduce the lattice parameters of the  $DO_{19}$   $Ti_3Al$  (see Table 1).

Table 1.

|             | L1 <sub>0</sub> TiAl |       |       |                 |                 |                 |                 |                 |                 | DO <sub>19</sub> Ti <sub>3</sub> Al |       |
|-------------|----------------------|-------|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-------------------------------------|-------|
|             | E <sub>c</sub>       | a     | c/a   | C <sub>11</sub> | C <sub>33</sub> | C <sub>12</sub> | C <sub>13</sub> | C <sub>44</sub> | C <sub>66</sub> | a                                   | c/a   |
| Calculation | 4.52                 | 4.02  | 1.017 | 149             | 165             | 88              | 92              | 61              | 57              | 5.7                                 | 0.804 |
| Experiment  | 4.52                 | 4.005 | 1.016 | 187             | 182             | 74.8            | 74.8            | 109             | 81.2            | 5.782                               | 0.801 |

Calculated and experimental values of the cohesive energy (eV), lattice parameters (Å) and elastic moduli (GPa). The experimental values of the cohesive energy have been taken from (Hultgren, et al. 1973) for the lattice parameters from (Pearson 1967) and for the elastic moduli from (Tanaka, et al. 1996).

The functional forms of the potentials are the same as in a number of previous cases in which the same scheme was employed (Ackland, et al. 1987; Vitek, et al. 1991). They are cubic splines so that the functions which make up the potentials are:

$$V_{AA}(r_{ij}) = \sum_{k=1}^6 a_k (r_k - r_{ij})^3 H(r_k - r_{ij}) \tag{3a}$$

$$\Phi_{AA}(r_{ij}) = \sum_{k=1}^2 A_k (R_k - r_{ij})^3 H(r_k - r_{ij})$$

where A represents either Ti or Al and

$$V_{TiAl}(r_{ij}) = \sum_{k=1}^4 a_k (r_k - r_{ij})^3 H(r_k - r_{ij}) \tag{3b}$$

$H(x)$  is the Heaviside step function and the corresponding parameters  $a_k$ ,  $A_k$ ,  $r_k$  and  $R_k$  are summarized in Table 2. The values of  $r_1$  and  $R_1$  represent cut-off radii of the corresponding potentials.

Since the potentials were constructed by fitting equilibrium properties of the  $L1_0$  lattice it is very important to test that spurious unphysical structures may not be stabilized in a defective environment. While this can never be done fully, two types of tests can be carried out that provide a reasonable assurance.

First, the stability of the fitted  $L1_0$  structure relative to other crystal structure with the same composition can be studied. In the present case we calculated the cohesive energies of fully relaxed B2 and structure '40' compounds and found 4.41eV and 4.50 eV, respectively. These are both lower than the cohesive energy of the  $L1_0$  structure. Structure B19 was also investigated but relaxation always transformed this structure into  $L1_0$ .

Secondly, the  $L1_0$  structure must be stable with respect to both small and large strains. The former is assured by the positive definiteness of elastic moduli. Clearly, an exhaustive test of the stability with respect to large strains cannot be made and the following two types of tests were performed. First, the energy of the structure was calculated as a function of strains corresponding to  $\pm 20\%$  changes in the lattice parameters  $a$  and

c. These calculations demonstrate that the energy increases for all the deformations applied and no local energy minima were found. The second is evaluation of  $\gamma$ -surfaces which are plots of energy vs displacement obtained by calculating the energy of the crystal cut along a crystallographic plane with one part displaced relative to the other part (see Vitek 1968, 1992). These calculations provide a test of the stability with respect to large shears. At the same time minima at these surfaces determine possible metastable planar faults of the stacking-fault type.

Using the constructed potentials the  $\gamma$ -surface for the (111) plane was calculated. (For more details see Girshick and Vitek 1995). The lowest energy minimum on this surface corresponds to the ideal  $L1_0$  structure. However, there are three different metastable stacking fault type defects on (111): the antiphase boundary (APB), the complex stacking fault (CSF) and the superlattice intrinsic stacking fault (SISF). The displacements

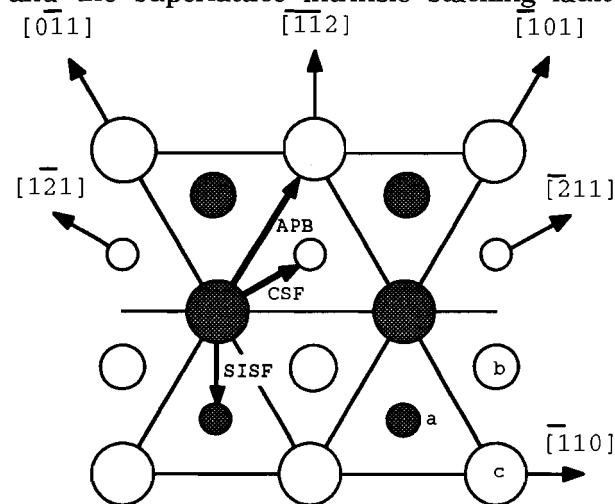


Fig. 1. The atomic arrangement in three (111) planes of the  $L1_0$  structure. The three layers are labeled a, b and c and distinguished by the size of the circles. Open circles represent Ti and shaded circles Al atoms, respectively.

related to these faults are  $1/2[\bar{1}01]$ ,  $1/6[\bar{2}11]$ , and  $1/6[11\bar{2}]$ . Fig. 1 shows the distribution of atoms in the (111) plane and the vectors corresponding to these faults; note that  $[\bar{1}01]$  and  $[\bar{1}10]$  vectors are not equivalent. The energies of these faults calculated using the potentials constructed are summarized in Table 3 and compared with values obtained using ab-initio LDA electronic structure calculations and with some experimental data.

Considering relatively large differences between different ab-initio calculations as well as between experimental values, the energies of the APB and the CSF are reproduced by the present potentials with sufficient precision. However, the calculated energy of the SISF is very low. The reason is that in this fault the separations  $\sim r$  of the first and second nearest neighbors remain practically the same as in the ideal lattice since the  $c/a$  ratio is very close to one. Thus in the central-force scheme only more distant neighbors contribute significantly to this energy. An appreciably higher energy of the SISF can be attained if the potentials are much longer ranged than the present ones which are cut between the third and fourth neighbors. Such potentials were constructed in the framework of the embedded atom method (EAM) by Rao, et al. (1991). However, a true physical reason for a much higher value of the SISF energy is most likely the directional, covalent component of the bonding in TiAl.

A discrepancy which is certainly related to the covalent character of bonding is the sign of the Cauchy pressures  $C_{12}$ - $C_{66}$  and  $C_{13}$ - $C_{44}$ . The experimental values of these pressures are -6.4 and -34.2 MPa, respectively, while the potentials give 31 and 30 MPa, respectively. It is a general feature of the Finnis-Sinclair type potentials and the EAM that negative Cauchy pressures cannot be reproduced. Such Cauchy pressures

signalize a contribution of covalent bonding which is not included into these schemes (Pettifor, et al. 1995). The importance of the covalent character of bonding in atomistic studies of dislocations and interfaces is not a priori clear and it will be discussed later in this paper.

Table 2.

|                | Ti              | Al              | Ti-Al         |
|----------------|-----------------|-----------------|---------------|
| a <sub>1</sub> | -0.892173390625 | 0.485497090961  | 0.0756562605  |
| a <sub>2</sub> | 1.261493718750  | -1.122148021598 | -0.1639193100 |
| a <sub>3</sub> | -0.340022937500 | 2.107197460791  | 0.3990835860  |
| a <sub>4</sub> | -0.162444984375 | -1.619069618174 | 0.2902223390  |
| a <sub>5</sub> | 1.164297312500  | 0.443144698322  |               |
| a <sub>6</sub> | 0.561266250000  | 0.301001333565  |               |
| A <sub>1</sub> | 0.621811359375  | 0.289298308255  |               |
| A <sub>2</sub> | -0.610332890625 | 0.074641404172  |               |
| r <sub>1</sub> | 4.88            | 4.9616175       | 4.70          |
| r <sub>2</sub> | 4.80            | 4.7793540       | 4.30          |
| r <sub>3</sub> | 4.48            | 4.4148270       | 3.70          |
| r <sub>4</sub> | 3.80            | 4.2528150       | 3.25          |
| r <sub>5</sub> | 3.20            | 3.6452700       |               |
| r <sub>6</sub> | 2.828428        | 3.0665096       |               |
| R <sub>1</sub> | 4.88            | 4.860360        |               |
| R <sub>2</sub> | 4.16            | 3.766779        |               |

Parameters of the  $V_{\text{TiTi}}$ ,  $\Phi_{\text{TiTi}}$ ,  $V_{\text{AlAl}}$ ,  $\Phi_{\text{AlAl}}$  and  $V_{\text{TiAl}}$  potentials. The radii  $r_i$  and  $R_i$  are in Å and coefficients  $a_i$  and  $A_i$  in eV/Å<sup>3</sup>.

Table 3.

| Type of the fault | Present potentials | Fu and Yoo <sup>a</sup> | Woodward and McLaren <sup>b</sup> | Experiment <sup>c</sup> |
|-------------------|--------------------|-------------------------|-----------------------------------|-------------------------|
| APB               | 275                | 510                     | 672                               | 250                     |
| CSF               | 275                | Not available           | 294                               | Not available           |
| SISF              | 2.9                | 90                      | 123                               | 140                     |

Energies of the APB, CSF and SISF on the (111) plane (mJm<sup>-2</sup>). (a) (Fu and Yoo 1990), (b) (Woodward, et al. 1991; Woodward and MacLaren 1996), (c) (Hug, et al. 1988).

### CORE STRUCTURE OF DISLOCATIONS

Owing to the tetragonality of the L1<sub>0</sub> structure, both ordinary dislocations and super-dislocations may be present on {111} type planes. For example, for the (111) plane (see Fig.1), slip along  $\bar{1}01$  or  $0\bar{1}1$  requires super-dislocations but only ordinary dislocations are needed for slip along  $\bar{1}10$ . As described in the Introduction both these types of dislocations may contribute to the plastic flow, together with twinning in

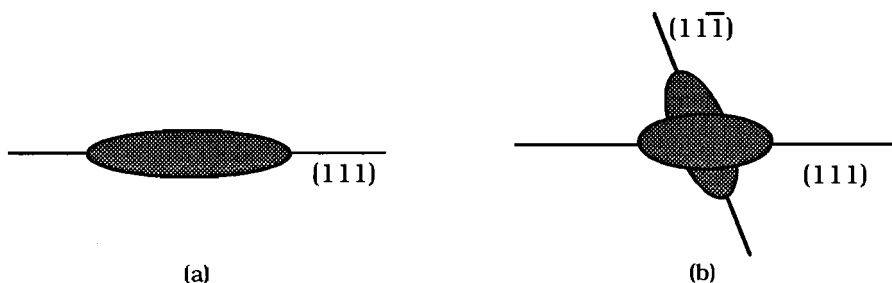


Fig. 2. Schematic pictures of the core structure of the  $\frac{1}{2}[\bar{1}10]$  screw dislocation in TiAl. (a) Planar core spread in the (111) plane. (b) Non-planar core spread in both (111) and  $(11\bar{1})$  planes.

the  $[\bar{1}1\bar{2}]$  direction. In order to investigate these deformation modes we have studied, using the potentials described in the preceding section, cores of three types of screw dislocations, ordinary  $\frac{1}{2}[\bar{1}01]$  and  $\frac{1}{2}[\bar{1}1\bar{2}]$  dislocations and  $[\bar{1}01]$  superdislocation (Girschick and Vitek 1995; Mahapatra, et al. 1995). Screw dislocations were considered since they lie parallel to short period directions and their slip plane is not well defined. Hence, they are most likely to display unusual core phenomena, in particular the non-planarity of the core spreading (Vitek 1992).

Two alternate core structures of the ordinary  $\frac{1}{2}[\bar{1}10]$  dislocation, shown schematically in Figs. 2a and b, respectively, were obtained using different starting configurations. The core shown in Fig. 2a is planar, spread into the (111) plane, while the core shown in Fig. 2b is non-planar, spread concomitantly into the (111) and  $(11\bar{1})$  planes and thus sessile. The sessile core is energetically favored since when a shear stress parallel to the  $[\bar{1}10]$  direction was applied in the (111) plane the planar core transformed into the non-planar one. However, in a similar study employing EAM type potentials (Rao, et al. 1991) it was found that the planar core configuration is favored (Simmons, et al. 1993; Rao, et al. 1995).

For  $[\bar{1}01]$  superdislocations two possible configurations of the core have also been found. They are shown schematically in Fig. 3 and correspond to two alternate dissociations of the superdislocation. The first (Fig. 3a) is planar and corresponds to the following splitting in the (111) plane  $[\bar{1}01] = \frac{1}{6}[\bar{2}11] + \text{SISF} + \frac{1}{6}[\bar{1}\bar{1}2] + \text{APB} + \frac{1}{2}[\bar{1}01]$ . The alternative configuration (Fig. 3b) is non-planar splitting according to the reaction  $[\bar{1}01] = \frac{1}{6}[\bar{1}\bar{1}2] + \frac{1}{3}[\bar{2}01] + \frac{1}{6}[\bar{1}12]$  into the (111) and  $(\bar{1}\bar{1}\bar{1})$  planes forming ribbons of the SISF in these planes. The partial dislocation with the Burgers vector  $\frac{1}{3}[\bar{2}01]$ , which lies at the intersection of the two  $\{111\}$  planes, is entirely immobile. The latter configuration is favored when the energy of the SISF is low but the planar structure is metastable and does not spontaneously transform into the sessile one.

The core structure of the  $\frac{1}{2}[\bar{1}1\bar{2}]$  dislocation is shown in Fig. 4. This core is spread into two adjacent (111) planes and the superlattice extrinsic stacking fault (SESF) is formed within the core. Such faults have, indeed, been observed earlier by electron microscopy (Hug, et al. 1986) and the recent HREM observation by Inkson and Humphreys (1995) can be interpreted as the dissociation shown in Fig. 4. This fault represents a microtwin, two atomic layers wide, and it may serve as a nucleus for twinning. Application of the corresponding external shear stress, indeed, led at high enough stresses to the growth of the twin in the  $[111]$  direction.

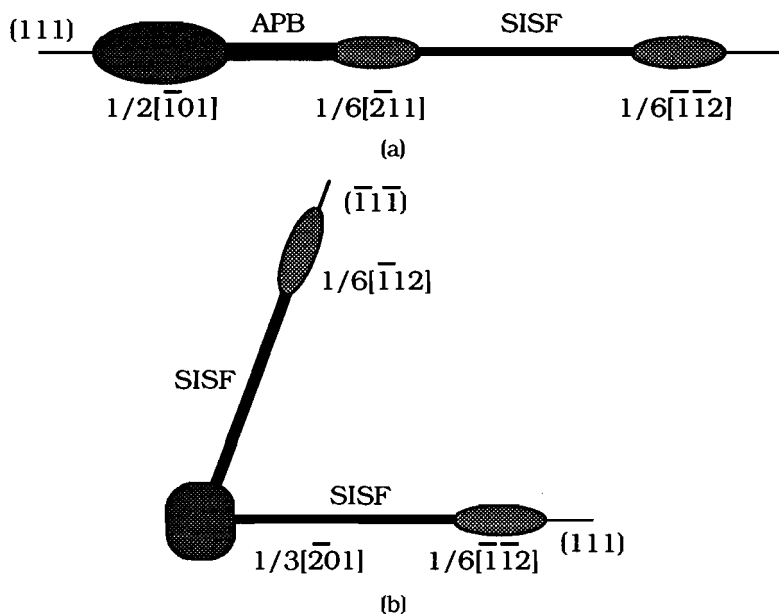


Fig. 3. Schematic pictures of the core structure of the  $\frac{1}{2}[\bar{1}01]$  screw superdislocation. (a) Planar core spread in the (111) plane; (b) Non-planar core spread in (111) and  $(\bar{1}\bar{1}\bar{1})$  planes.

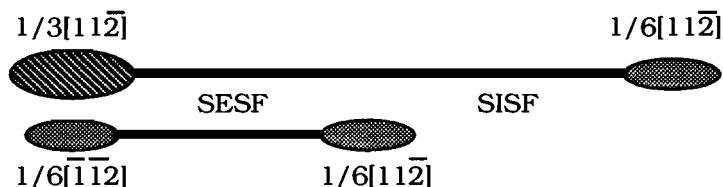


Fig. 4. Schematic picture of the core structure of the  $\frac{1}{2}[\bar{1}1\bar{2}]$  screw dislocation.

Results of these calculations may provide a basis for understanding the deformation modes in TiAl. First, based on the results of the simulations, we can conclude that ordinary  $\frac{1}{2}[\bar{1}10]$  dislocations have non-planar cores when in screw orientation and require substantial thermal activation to attain a significant mobility. Hence, these dislocations will control plastic behavior only if other alternate modes are not available. In PST crystals the dominant mode at low temperatures is twinning. This can be understood if we assume that the energies of both the SISF and the coherent twin boundary increase rapidly with increasing aluminum content and are relatively low in nearly stoichiometric PST crystals. The sessile form of the superdislocations, corresponding to splitting into non-parallel  $\{111\}$  planes with the SISF, will then be preferred in PST crystals. At the same time the twin boundary energy is also low and wide splitting of the  $\frac{1}{2}[\bar{1}1\bar{2}]$  dislocations on (111) planes can be expected. These dislocations then serve as nuclei for twinning which thus becomes the dominant deformation mode, as observed. At high temperatures both the ordinary and superdislocations with non-planar cores become more mobile owing to thermal activations.

In single phase alloys which are Al rich, the SISF energy is high and thus the difference between planar and non-planar cores of the superdislocations will not be large. Hence, even if the sessile form is energetically favored, the superdislocations may possess metastable planar

cores when gliding at room temperature. However, as the temperature increases, superdislocations will be transforming into energetically more favorable sessile configurations involving SISF on both (111) and ( $\bar{1}\bar{1}\bar{1}$ ) planes. Ordinary dislocations will then dominate the slip but since glide will still be more difficult at high temperatures than at low temperatures, twinning may occur as an alternative yielding mechanism. This dislocation behavior may also explain the anomalous increase of the yield stress with increasing temperature.

## INTERFACES IN TWO-PHASE TiAl

### Atomic structure and energy of lamellar interfaces

There are two primary types of lamellar interfaces in multiphase TiAl: TiAl/TiAl interfaces between two twin-related lamellae with  $L1_0$  structures, and TiAl/Ti<sub>3</sub>Al interfaces between lamellae with  $L1_0$  and  $DO_{19}$  structures, respectively. In the former case the interfacial planes are (111) and  $\langle 1\bar{1}0 \rangle$  vectors in adjacent lamellae are parallel. In the latter case interfacial planes are (111) in TiAl and (0001) in Ti<sub>3</sub>Al and  $\langle 1\bar{1}0 \rangle$  and  $\langle 11\bar{2}0 \rangle$  vectors in adjacent lamellae are parallel.

The crystallography, morphology and distribution of lamellar interfaces have been studied by TEM (Blackburn 1970; Schwartz and Sastry 1989; Inui, et al. 1992b). Both TiAl/TiAl and TiAl/Ti<sub>3</sub>Al interfaces can be divided into two groups. The first group is characterized by coherent matching of columns of Ti atoms in the upper  $L1_0$  lamella to columns of Ti atoms in the lower lamella which is either  $DO_{19}$  or  $L1_0$ . In the second group columns of Al atoms in the upper  $L1_0$  lamella coherently match columns of Ti atoms in the lower lamella which is either  $DO_{19}$  or  $L1_0$ . The second group can also be regarded as related to the first group by displacing the  $L1_0$  grain by the corresponding APB vector in the (111) plane. In the following we concentrate on the atomic structure of TiAl/TiAl interfaces which are always in majority owing to the near equiatomic composition of TiAl alloys. However, atomistic studies of TiAl/Ti<sub>3</sub>Al interfaces have also been made recently (Siegl 1996).

There are three geometrically distinct variants of twin-related TiAl/TiAl interfaces which can be described, using the notation of Fig. 1, as follows: (i) Twin in which the  $[\bar{1}10]$  direction of the matrix is antiparallel to the  $[\bar{1}10]$  direction of the twin. (ii) 120° rotational fault for which the  $[1\bar{1}0]$  direction of the matrix is parallel to the  $[10\bar{1}]$  direction of the twin. (iii) Pseudotwin for which the  $[1\bar{1}0]$  direction of the matrix is antiparallel to the  $[10\bar{1}]$  direction of the twin. It follows from the symmetry that structural variants with the (111) APB type displacement are equivalent to the undisplaced ones for the 120° rotational fault and the pseudotwin. However, the twin with the APB type shift is not equivalent to the ordered twin. In fact, both coherent and shifted ordered twin boundaries have been observed (Ricolleau, et al. 1994) and it is the latter boundary which will be discussed in more details below.

While the  $c/a$  ratio deviates only by about 2% from one, it is not ideal and this has significant consequences for the pseudotwin and 120° rotational fault. It results in a misfit at these interface which is compensated by a network of misfit dislocations (Kad and Hazzledine 1992). In contrast, the non-ideal  $c/a$  ratio does not invoke any misfit at ordered twins. However, the misfit dislocations present at interfaces are about fifty lattice spacings apart and thus there are large areas between them where the matching of the lamellae is coherent. The structures and

energies of these coherent regions were calculated using modified Finnis-Sinclair type potentials fitted to obtain  $c/a=1$  (Siegl 1996).

The lowest energy structure is the ordered twin, as could be expected. This is followed by the  $120^\circ$  rotational fault and the pseudotwin. The energy of the twin with the APB type displacement is twice as high as the energy of the pseudotwin. This order of energies is consistent with estimates employing a geometrical bond-counting model (Inui, et al. 1992b) and ab-initio LDA based calculations (Fu and Yoo 1990; Woodward, et al. 1991; Woodward and MacLaren 1996). Unfortunately, the energy of the twin is very much underestimated in the central-force scheme, similarly as the energy of the SISF; a higher value can be expected if the non-central character of atomic bonding were considered. Hence, the ratios of the energies of different TiAl/TiAl interfaces cannot be directly determined. Nevertheless, these calculations have been employed to rationalize the measurements of the angles of surface grooves the magnitudes of which are related to interfacial energies (Lu, et al. 1996).

**Atomic structure of the ordered twin with APB type displacement**

In this interface, whose geometrically constructed structure is shown in Fig. 5a, the boundary plane is a 'color reversing mirror plane' reflecting Ti into Al and vice versa. As mentioned above, the non-ideal  $c/a$  ratio does not invoke any misfit across this interface and thus its structure can be studied straightforwardly using the Finnis-Sinclair type potentials introduced in this paper. Such calculation was carried out by minimizing its energy with respect to the positions of individual atoms and relative rigid body translations of adjoining lamellae. The relaxations lead to only very small displacements of atoms away from their geometrically determined positions and they are principally associated with a small,  $0.06\text{\AA}$ , rigid body displacement of the adjoining lamellae in the  $[11\bar{2}]$  direction, parallel to the boundary plane. The physical reason for this relaxation is the following: In the symmetric boundary the nearest neighbor Ti-Al separations across the interface are smaller than Ti-Ti and Al-Al separations, while in the perfect lattice, owing to the non-ideal  $c/a$  ratio, Ti-Ti and Al-Al nearest neighbors are closer to each other than Ti-Al neighbors. The small relative displacement of the lamellae restores the correct sequence of neighbor separations.

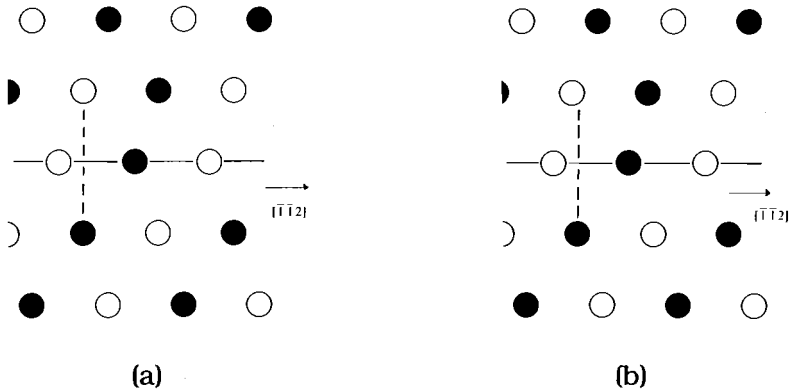


Fig. 5. Relaxed structure of the ordered twin with APB type displacement. (a) Finnis-Sinclair type potentials. (b) Full-potential LMTO method.



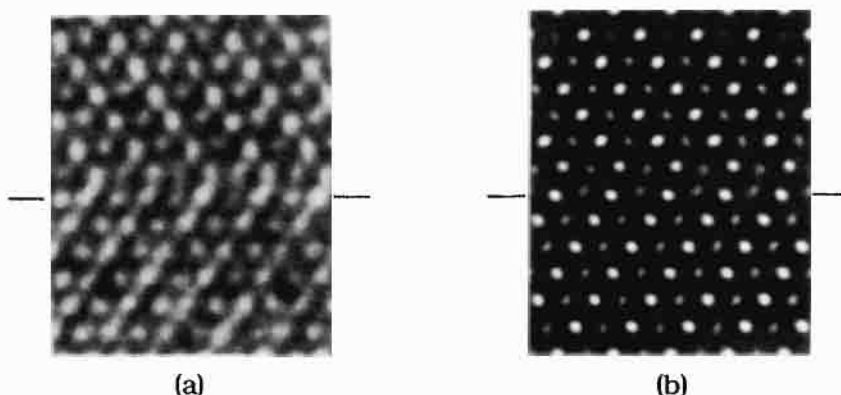


Fig. 6. HREM image of the ordered twin with APB type displacement. (a) Experiment. (b) Simulation based on the structure obtained using the full-potential LMTO method.

The atomic structure of this boundary has also been explored by HREM. The observations were carried out using the JEOL JEM-4000EX electron microscope operated at 350 kV. The observed HREM image is shown in Fig. 6a. The most interesting feature is a clearly visible asymmetry of the interfacial structure which is related to the shift of the upper lamella relative to the lower one in the  $[11\bar{2}]$  direction. However, the HREM image of the calculated structure, simulated using the multi-slice method (Self and O'Keefe 1988), does not display any visible loss of mirror symmetry across the boundary plane. Presumably, the displacement of 0.06 Å is too small to be discernible in the simulated image (Luzzi 1991). Therefore, the observed displacement is substantially larger than that found in the calculations.

The most likely reason is the inadequacy of the central-force potentials which exclude any covalent type bonding. In order to investigate this possibility the structure of the twin boundary with the APB type shift was studied using the ab-initio LDA based full-potential LMTO method (Methfessel 1988; Methfessel, et al. 1989) which automatically includes any possible directional bonding<sup>2</sup>. Only a one-dimensional relaxation was carried out. Starting with the structure obtained using the Finnis-Sinclair potentials, the upper lamella was shifted in the  $[11\bar{2}]$  direction with respect to the lower lamella in steps and the interfacial energy calculated as a function of this shift; no additional relaxation of individual atoms was allowed. Minimum energy configuration corresponds to the shift by 0.2 Å and the structure corresponding to this minimum of the energy is displayed in Fig. 5b. The asymmetry across the interface is now clearly visible. The simulated HREM image of this

<sup>2</sup> Since the full-potential LMTO is a  $\mathbf{k}$ -space method the supercell geometry was used and this introduces periodicity in the direction perpendicular to the interface. Therefore, an array of interfaces is in fact studied and their separation has to be large enough to avoid their interaction. In the present calculations it was found that three atomic layers provided sufficient screening and thus six atomic layers in the supercell were used. The following parameters have been used in these calculations: (i) twenty two linear muffin-tin orbitals per atom, (ii) the cutoff radius for augmentation and charge density expansion  $l = 4$ , (iii) the Hamiltonian was diagonalized in approximately 70  $\mathbf{k}$ -points in the irreducible wedge of the first Brillouin zone, (iv) the local exchange and correlation potential of Hedin and Lundqvist (1971) was used. This choice of parameters results in the convergence of the total energy better than 0.05 mRy per atom.

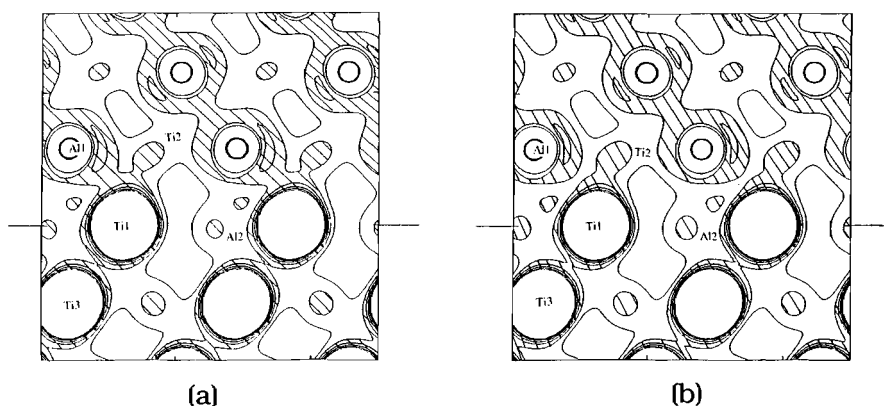


Fig. 7. Maps of the electronic charge density in the  $(1\bar{1}0)$  planes in the ordered twin with  $(111)$  APB type displacement. The hatched areas correspond to the charge density higher than 0.03 electrons per cubic Bohr. The charge density differences between two successive contours of the constant charge density are 0.005 electrons per cubic Bohr. Atoms in the two successive  $(1\bar{1}0)$  planes are denoted as Ti1, Al1, and Ti2, Al2, respectively. (a) Structure calculated using the Finnis-Sinclair type potential. (b) Structure calculated using the full-potential LMTO method.

interfacial configuration is shown in Fig. 6b. The agreement between the simulated and experimental image is remarkable. Both images exhibit the asymmetry across the interface and the ladder-type contrast along the interface is fully reproduced. The non-central, covalent type bonding must obviously play an important role at the interface and this can be analyzed with the help of electronic charge density plots that were calculated in the framework of the full-potential LMTO method.

In the perfect lattice the dominant feature of the electron distribution is the formation of the covalent, directional bond between Ti atoms produced by the electrons associated with d-orbitals. The concentration of charge between adjacent Al atoms corresponds to  $p_x$  and  $p_y$  electrons, but these electrons are spatially more dispersed than the d-electrons between titanium atoms. Significantly, there is no indication of a localized charge build-up between adjacent Ti and Al atoms (Fu and Yoo 1990; Woodward, et al. 1991; Song, et al. 1994). The charge densities in  $(1\bar{1}0)$  planes are shown in Fig. 7a and b for the structures relaxed using the Finnis-Sinclair type potentials and the full-potential LMTO method, respectively.

A pronounced build-up of the electronic charge between Ti and Al atoms adjacent to each other across the boundary is seen in Fig 7a (Ti1 and Al1). This suggests formation of a covalent bond between Ti and Al in the boundary region of the symmetrical structure. In contrast, in the asymmetric structure, no pronounced charge build-up occurs between Ti and Al atoms across the boundary (Fig. 7b) and the charge concentration between the atoms Ti1 and Ti2 is higher in this structure than in the symmetric structure suggesting stronger Ti-Ti bonds of the d character. Hence, the asymmetrical structure exhibits the bonding across the interface which is appreciably more similar to that found in the bulk than the symmetrical structure. The main feature is the covalent type bond formed by Ti d electrons which is preserved at the interface in the asymmetrical structure but replaced by formation of a covalent type bond between Ti and Al in the symmetrical structure.

## CONCLUSIONS

In this paper we have presented atomistic studies of dislocations and lamellar interfaces in TiAl which crystallizes in the tetragonal  $L1_0$  structure. For this purpose we first constructed a central-force Finnis-Sinclair type many body potentials. This scheme, together with the EAM, has been very successful in studies of dislocations and grain boundaries in close packed metals and metallic compounds. Notable are studies in noble metals, copper-bismuth and nickel-aluminum alloys (Finnis and Rühle, 1993; Yan et al., 1993; Yan and Vitek, 1995) in which the bonding is principally metallic. However, while TiAl is almost close-packed, the bonding is not purely metallic and its covalent component can be significant. This has been revealed in ab-initio electronic structure calculations (Fu and Yoo 1990; Woodward, et al. 1991; Song, et al. 1994) and is reflected in the negative Cauchy pressures. Hence, it is important to consider the applicability and limitations of the central-force potential scheme which is, of course, much more efficient computationally than ab-initio studies.

In the case of dislocations calculations employing central-force potentials revealed possible core configurations and suggested that the most important factor controlling the deformation modes in TiAl is the dependence of the SISF and twin boundary energy upon the aluminum content. This idea is, indeed, supported by recent experimental investigations which propound that the propensity for twinning decreases rapidly with increasing aluminum concentration, independently of the presence of interfaces (Mahapatra, et al. 1995; Yamaguchi, et al. 1995). Hence, calculations using a relatively simple central-force scheme have been able to identify the most important factor controlling the deformation modes in TiAl. However, the dependence of the SISF and twin boundary energy on the aluminum concentration cannot be analyzed in the framework of these potentials and more fundamental quantum mechanics based studies of alloying effects are needed. In fact, the central-force character of these potentials is the main reason why the energies of the SISF and twin boundary are unrealistically low in this scheme.

Similarly, in studies of lamellar interfaces the calculations using the central-force potentials predict correctly the order of energies for different interfaces but their ratios cannot be determined since the energy of the ordered twin is unphysically low, similarly as that of the SISF. Notwithstanding, the situation is more complex in the case of interfaces. It has been demonstrated that the atomic structure of an ordered twin with APB type displacement is not predicted correctly in the framework of central-forces and that it is the formation of strong Ti-Ti covalent bonds across the interface which dominates the structure. This character of bonding in TiAl is likely to be even more important in more complex interfaces and it cannot be excluded that it affects directly dislocation cores.

Hence, a further advancement in studies of dislocations and interfaces in TiAl requires introduction of non-central forces into atomistic calculations. This character of bonding is, of course, included in ab-initio electronic structure calculations but such calculations are still not feasible on the scale needed when investigating dislocations and interfaces. Empirical attempts to include directionality of bonding have been made (Panova and Farkas 1995) but only employment of quantum mechanics based potentials can reveal the effects of non-central forces unambiguously. Such potentials have been emerging recently but have not yet been employed extensively in studies of lattice defects (Aoki and Pettifor, 1994; Manh et al., 1995; Pettifor et al., 1995). Incorporation of

such potentials into atomistic studies of lattice defects is an important challenge for future research.

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# A SIMPLE APPROACH TO THE ENERGETICS OF SURFACE DEFECTS IN TRANSITION METALS

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## INTRODUCTION

The last twenty years have seen a rapid development of surface physics. In particular, the properties of clean perfect surfaces (with two-dimensional periodicity) are henceforth well known and understood. In recent years, the focus has been put onto surfaces with defects (adatoms, steps, vacancies, impurities...) which can now be investigated experimentally due either to the progress of old techniques (field ion microscopy or He diffraction, for instance) or to the rapid development of new methods (STM, AFM, SEXAFS...).

On the theoretical point of view, the presence of defects sets difficult problems since it breaks the two-dimensional periodicity of the surface and induces local atomic relaxations. As a consequence, the *ab initio* methods become rapidly intractable at least for understanding trends which needs to investigate a large number of systems. Thus, a variety of empirical and semi-empirical schemes has been developed. Among them the tight-binding method plays an important role and has been extensively applied to the energetics of transition metals and semi-conductors. In this method total energies are expressed as a sum of the band structure energy and a short range repulsive interaction between atoms. Indeed, the valence band of these elements is correctly described by a tight-binding hamiltonian and the

repulsive energy, which was first introduced empirically, has now received strong support from ab initio methods based on the local density approximation<sup>1</sup>.

Here, we will first briefly recall the principles of this method in the case of transition metals. Then we will apply it to two illustrative examples : the surface segregation energy of an impurity in a pure host and the growth of adislands on FCC(111) surfaces of the same chemical species.

## TOTAL ENERGY CALCULATIONS IN THE TIGHT-BINDING APPROXIMATION

We will limit ourselves here to transition metals. It is well known that in these metals, the cohesive properties are largely dominated by the valence d electrons, and consequently, sp electrons can be neglected save for the elements with an almost empty or filled d valence shell<sup>2</sup>. Since the valence d atomic orbitals are rather localized, the d electronic states in the solid are well described in the tight-binding approximation. In this approximation, the cohesive energy of a bulk crystal is usually written as :

$$E_{\text{tot}} = E_{\text{band}} + E_{\text{rep}} \quad (1)$$

$E_{\text{band}}$  is the attractive part of the energy due to the broadening of the d valence energy level into a band, ie :

$$E_{\text{band}} = \int^{E_F} (E - E_d) \mathcal{N}(E) dE \quad (2)$$

$E_d$  is the center of gravity of the d band,  $\mathcal{N}(E)$  the total density of states and  $E_F$  the Fermi energy.

$E_{\text{rep}}$  is a pairwise repulsive term which implicitly includes the effect of electron-electron interactions which have been counted twice in  $E_{\text{band}}$  and of ion-ion repulsions<sup>1</sup>. It is usually assumed to be of the Born-Mayer type<sup>3, 4</sup>, i. e. :

$$E_{\text{rep}} = \sum_{i,j < i} A \exp \left[ -p(R_{ij} / R_0 - 1) \right] \quad (3)$$

where A and p are parameters characteristic of the considered metal,  $R_{ij}$  is the distance between atoms i and j, and  $R_0$  is the equilibrium interatomic distance in the bulk.

Let us now discuss the calculation of  $E_{\text{band}}$  in more detail. The tight-binding hamiltonian<sup>3,4</sup> is written as :

$$H = T + \sum_i V(\mathbf{r} - \mathbf{R}_i) = T + \sum_i V_i \quad (4)$$

T is the kinetic energy operator and  $V(\mathbf{r} - \mathbf{R}_i)$  is the atomic potential centered at site i. The set of atomic d orbitals  $\phi_\lambda(\mathbf{r} - \mathbf{R}_i) = |i \lambda\rangle$



$(\lambda = xy, yz, zx, x^2 - y^2, 3z^2 - r^2)$  centered at each site  $i$  is assumed to provide a complete orthonormal basis set on which the eigenfunctions  $|n\rangle$  of energy  $E_n$  can be expanded, i. e. :

$$|n\rangle = \sum_{i\lambda} c_{i\lambda}(E_n) |i\lambda\rangle \quad (5)$$

In this basis  $H$  is defined by :

- its interatomic matrix elements, i. e., the hopping integrals  $\langle i\lambda | H | j\mu \rangle$  ( $i \neq j$ ) which determine the band width  $W$  and depend on the direction cosines of  $\mathbf{R}_{ij}$  and on the Slater-Koster parameters  $dd\lambda$  ( $\lambda = \sigma, \pi, \delta$ ). The variation of these parameters with distance is taken to be exponential :

$$dd\lambda = dd\lambda_0 \exp[-q(\mathbf{R}_{ij} / R_0 - 1)] \quad (6)$$

and they are neglected beyond the nearest neighbours in FCC crystals and beyond the next nearest neighbours in BCC crystals. The ratio  $dd\sigma/dd\pi$  and  $dd\delta/dd\pi$  do not vary substantially along a transition series. Therefore, we can take them as constants when studying trends along the transition series. Within this approximation we are left with the bandwidth  $W$  as a single parameter. The numerical values of the ratios  $dd\sigma/dd\pi$  and  $dd\delta/dd\pi$  are estimated from fits to band structure calculations at high symmetry points of the Brillouin zone.

- its intraatomic matrix elements, i. e., the effective atomic levels,  $\langle i\lambda | H | i\mu \rangle = E_{di} \delta_{\lambda\mu}$  which, in the bulk, are all equal and correspond to the center of gravity of the  $d$  band.

The presence of a defect in the lattice (impurity, surface, vacancy...) breaks the symmetry and induces perturbations of the electronic structure in its vicinity. Thus it is convenient to introduce the concept of local density of states<sup>4</sup> (LDOS) at site  $i$  :

$$\begin{aligned} n_i(E) &= 2 \sum_{\lambda,n} c_{i\lambda}^*(E_n) c_{i\lambda}(E_n) \delta(E - E_n) \\ &= n_0(E) + \Delta n_i(E) \end{aligned} \quad (7)$$

where  $n_0(E)$  is the bulk density of states and  $\Delta n_i(E)$  the perturbation of the LDOS at site  $i$  which is only noticeable near the defect ( $n_i(E)$  is here normalized to 10). The existence of a non-vanishing  $\Delta n_i(E)$  is the region of the defect produces a redistribution of charge and, consequently, a perturbation of the potential on the atoms close to the defect. Ideally, the change in charge density and potential should be calculated self-consistently but the range of the screening in transition metals being of the order of an interatomic distance, a local charge neutrality condition, i. e. :

$$\int_{-\infty}^{E_F} \Delta n_i (E, \dots, \Delta V_j, \dots) dE = 0 \quad (8)$$

in a good approximation to determine the shifts  $\Delta V_i$  of the effective atomic levels at each site  $i$ .

Under this assumption the energy of the system with a defect relative to a bulk with the same number of atoms is :

$$\Delta E = \Delta E_{\text{band}} + \Delta E_{\text{rep}} \quad (9)$$

with

$$\Delta E_{\text{band}} = \sum_{i \in C} \left[ \int_{-\infty}^{E_F} E \Delta n_i (E, \dots, \Delta V_j, \dots) dE - N_i \Delta V_i \right] \quad (10)$$

$N_i$  is the number of  $d$  electrons of the atom at site  $i$  and the second term in the bracket avoids the double counting of the change in the electron-electron interactions that are responsible for the shift of the atomic level  $\Delta V_i$ .  $C$  is the set of atoms significantly perturbed by the defect and  $\Delta E_{\text{rep}}$  is the perturbation of the pair wise repulsive interactions.

The LDOS are calculated using the Green operator  $G(z) = (z - H)^{-1}$  :

$$\begin{aligned} n_i(E) &= -\frac{2}{\pi} \Im \sum_{\lambda} \langle i|\lambda| G(E + i0^+) |i\rangle \\ &= -\frac{2}{\pi} \Im \sum_{\lambda} G_{ii}^{\lambda\lambda}(E + i0^+) \end{aligned} \quad (11)$$

The quantity  $G_{ii}^{\lambda\lambda}(z)$  can be easily evaluated, even in the presence of defects, by using a continued fraction technique which does not assume any periodicity of the system <sup>3,4,5</sup>. In practice  $n$  levels of the continued fraction are computed exactly and the remaining part of the continued fraction is replaced by the usual square root terminator which corresponds to using the asymptotic values for the remaining coefficients. Note that these asymptotic values are fixed by the band limits which are known exactly in many cases. The more accurate the calculation of  $\Delta E$  is required to be, the more exact moments  $\mu_p^i$  :

$$\mu_p^i = \int_{-\infty}^{\infty} E^p n_i(E) dE \quad (12)$$

of the LDOS need to be included. It has been shown that if the  $G_{ii}^{\lambda\lambda}$  have  $n$

exact levels in the continued fraction, the  $2n$  first moments of the LDOS  $n_i(E)$  are exact.

A very simplified approach exists in the literature in which the exact LDOS are replaced by constant densities of states with the same first three moments :  $\mu_0^i = 10$ ,  $\mu_1^i = E_d + \Delta V_i$  and  $\mu_2^i$ . In this scheme,  $\Delta E$  can be written as <sup>6</sup> :

$$\Delta E = \sum_i E_i = \sum_i \Delta \left\{ \sum_{j < i} A \exp[-p(R_{ij}/R_0 - 1)] - B \sqrt{\sum_{j \neq i} \exp[-2q(R_{ij}/R_0 - 1)]} \right\} \quad (13)$$

where the parameters  $A$ ,  $B$ ,  $p$ ,  $q$  are usually fitted to bulk properties and the interaction between atoms  $i$  and  $j$  is neglected beyond some cut-off distance.

This expression is simple enough to lead to analytical calculations. It has the advantage of taking into account the non pairwise character of the attractive part of the energy which is obvious from the presence of the square root in the second term of (13). Therefore, when the atom  $i$  has  $Z_i$  neighbours, all at the same distance,  $E_i$  is proportional to  $\sqrt{Z_i}$ . Thus the energy gain when the coordination number of an atom is increased by one becomes smaller the more this atom is coordinated, i. e., there is a saturation effect in the lowering of energy when adding bonds. However, in this approximation, when two atoms have the same neighbour environment, they contribute to the total energy by the same amount since their LDOS have the same first three moments ( $\mu_0$ ,  $\mu_1$ ,  $\mu_2$ ). This is only approximate since it can be shown by including more moments that the difference in their contribution to the total energy changes sign as a function of the band filling<sup>3</sup>. This will be illustrated in the second example given in the following and may give rise to noticeable effects when  $\Delta E$  is small.

Finally, it is possible to perform molecular dynamic simulations in which the forces are obtained from the tight-binding model. Indeed, the simplified energy expression (13) has all the advantages of empirical potentials and can handle several thousands of atoms. However, more accurate calculations can be done in the full tight-binding theory by using the fictitious Lagrangian method of Car and Parrinello<sup>7</sup>. In this method the coefficients  $c_{i\lambda}$  corresponding to occupied states are taken as "electronic coordinates" and obey a "classical" equation of motion<sup>8</sup>. Nevertheless this scheme is much more time consuming than the previous one and, consequently, the number of atoms is reduced to a few hundreds. This is still an order or magnitude larger than in *ab initio* calculations.

## APPLICATIONS

We will now present two applications of the above method

- the calculation of the segregation energy of a single impurity at the surface of a pure BCC host<sup>9</sup> and the modification of this energy due to an adsorbed Oxygen layer<sup>10</sup>.

- the study of the relative stability of very small (1 to 3 atoms) adislands on the (111) surface of FCC transition metals of the same chemical species<sup>11</sup>.

### Surface segregation energy

We will limit ourselves to the surface segregation energy of an impurity of atomic number  $Z + 1$  in a BCC matrix of atomic number  $Z$  and study the variation of this energy as a function of the number  $N_d$  of  $d$  electrons per atom in the  $d$  band of the transition metal  $Z$ .

This case is particularly interesting since the surface segregation energy can be directly compared to surface core level binding energy shifts (SCLS) measurements. Indeed, if we assume that the excited atom (i. e., with a core hole) is fully screened and can be considered as a  $(Z + 1)$  impurity (equivalent core approximation), then the SCLS is equal to the surface segregation energy of a  $(Z + 1)$  atom in a  $Z$  matrix<sup>12</sup>. In this approximation the SCLS is the same for all the core states of an atom.

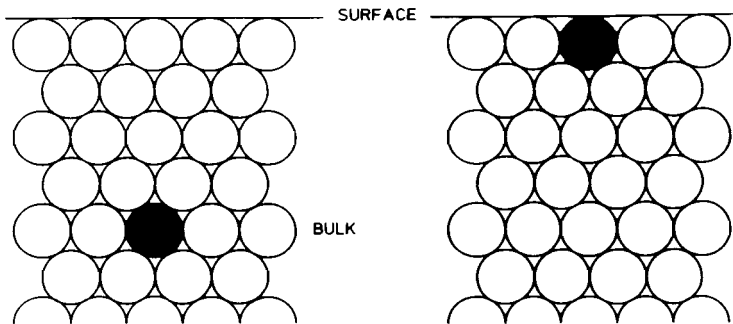


**Figure 1.** Surface segregation of an impurity of atomic number  $Z + 1$  (full circle) in a matrix of atomic number  $Z$  (open circles)

The calculation of the surface segregation energy follows the method explained above. Assuming that the repulsive energy between two neighbouring atoms is the same for a  $Z - (Z + 1)$  pair as for a  $Z - Z$  pair, the segregation energy of a  $Z + 1$  atom in layer  $p$ ,  $E_{\text{segr}}(S_p)$ , ( $p = 0$  : surface layer) is only due to the variation of the band contribution between the two systems shown in Fig. 1. The quantity  $\Delta V_i$  is determined by the local neutrality condition, i. e., for a host atom by (8) and for the impurity by :

$$\int_{-\infty}^{E_F} n_1(E, \Delta V_1, \Delta V_2 \dots) dE = N_1 \quad (14)$$

where  $N_1 = N_d(Z + 1)$  is the number of  $d$  electrons of the impurity.

The LDOS have been calculated using 10 exact levels in the continued fraction expansion of the Green functions. For clean surfaces the quantities  $\Delta V_i$  are the same for all atoms in the same plane ; they have been determined up to  $p = 2, 4, 6$  for the (110), (100) and (111) surfaces, respectively, and neglected beyond. The cluster C includes the atoms located at the site occupied by the impurity and at all the neighbouring sites up to the fourth nearest neighbour.

The surface have been assumed, unrelaxed and unreconstructed. The d band filling has been varied in the range  $(3 - 4.6)e^-$  per atom which includes the BCC transition metals and, in particular, the case of Ta and W. The results are displayed in Fig. 2. As often assumed, we have taken  $N_d(Z + 1) - N_d(Z) = 1.1$ . However, as shown in Fig. 2, changing this difference to 1 modifies only slightly the numerical results.

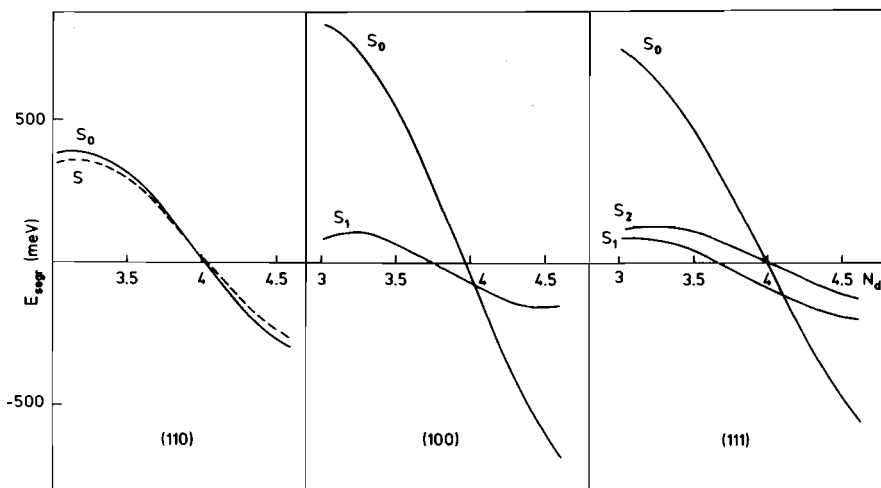


Figure 2. Segregation energy in layer  $S_p$  ( $p = 0$  surface layer...) of a transition metal impurity of atomic number  $Z + 1$  (d band-filling :  $(N_d + 1.1)e^-/\text{atom}$ , full curves ;  $(N_d + 1)e^-/\text{atom}$ , dashed curve) in a BCC transition metal matrix of atomic number  $Z$  (d band-filling :  $N_d e^-/\text{atom}$ ) for various crystallographic orientations of the surface

As expected from the equivalent core approximation, the segregation energy follows the same behaviour as experimental SCLS : it is positive at the beginning of the series and changes sign for a d band filling between those of Ta and W. Indeed, it is commonly admitted that the sign of the surface segregation energy is fixed by the relative values of the clean surface energies  $E_s(Z)$  and  $E_s(Z + 1)$  of the elements  $Z$  and  $Z + 1$ . The function  $E_s(Z)$  being at a maximum in the middle of the series, a change of sign of  $E_s(Z + 1) - E_s(Z)$  should occur in the studied range of d band fillings. The segregation energy increases with the number of broken bonds at the surface and it is still significant on the first sublayers of open surfaces. The numerical agreement with measured SCLS is very satisfactory<sup>9</sup>.

In the case of W(110) ( $N_d = 4.4e^-/\text{atom}$ ), we have also calculated the modification of the surface segregation energy of a Re impurity when a  $p(2 \times 1)$  overlayer of oxygen is present at the surface (Fig. 3). Then, there are two geometrically inequivalent atomic rows, labelled a and b, of W atoms on the surface (and in the sublayers). However, the modification of their effective atomic levels relative to the bulk is vanishingly small beyond the second

layer. We have found that the surface segregation energy decreases in absolute value by 380 meV and 250 meV for a Re atom at the surface in row a and b, respectively. Note that this is consistent with the decrease of the oxygen chemisorption energy when going from tungsten to rhenium.

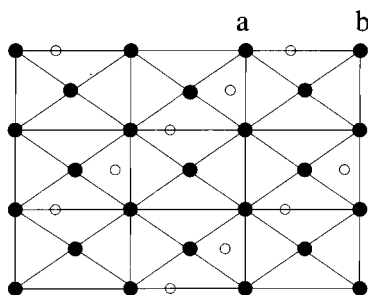


**Figure 3.** The  $p(2 \times 1)$  O overlayer on W(110) : W surface atoms (full circles), O atoms (open circles)

### Stability of adislands on the (111) surface of FCC transition metals

Crystal growth has, apart from its basic surface science interest, important applications in technology for instance in microelectronics, optoelectronics, recording... However, even the simplest case of homoepitaxy is not perfectly understood. In particular, growth on FCC (111) transition metal surfaces raises some interesting questions.

First, there exists two types of adsorption sites : the normal site (N or FCC) which continues the bulk regular stacking, and the fault site (F or HCP) which introduces a stacking fault. This problem is clearly connected to that of the relative stability of FCC and HCP phases which is known to obey systematic trends as a function of the d band-filling but these trends may be modified by the lowering of symmetry at the surface. Indeed, in a previous study, we showed that a single Ir adatom sits at a fault site while a complete monolayer does not introduce any stacking fault. Thus, an inversion of relative stability from fault to normal site is expected to occur when the size of adislands increases. This has been observed experimentally using field ion microscopy by Wang and Ehrlich<sup>13</sup>. They found that there is indeed a transition from fault to normal adsorption sites when the size of the Ir adclusters reaches 3 atoms.

Second, as their size increases, these adislands can be limited by two kinds of close-packed atomic rows corresponding to two different types of microfacets : (001) for type A and (111) for type B. In the above mentioned experiments, Wang and Ehrlich<sup>13</sup> have shown that triangular Ir trimers with type B borders are energetically favoured.

Here, we address the more general question of the relative stability of monomers, dimers and triangular trimers on the (111) surface of FCC transition metals of the same chemical species as a function of the d band filling  $N_d$ . All possible atomic configurations of the systems are considered ; monomers and dimers at sites N and F, triangles with A and B borders at sites N and F (Fig. 4). The d band-filling includes the range of stability of the FCC phase ( $N_d > 7.5e^-/\text{atom}$ ). The densities of states are obtained from

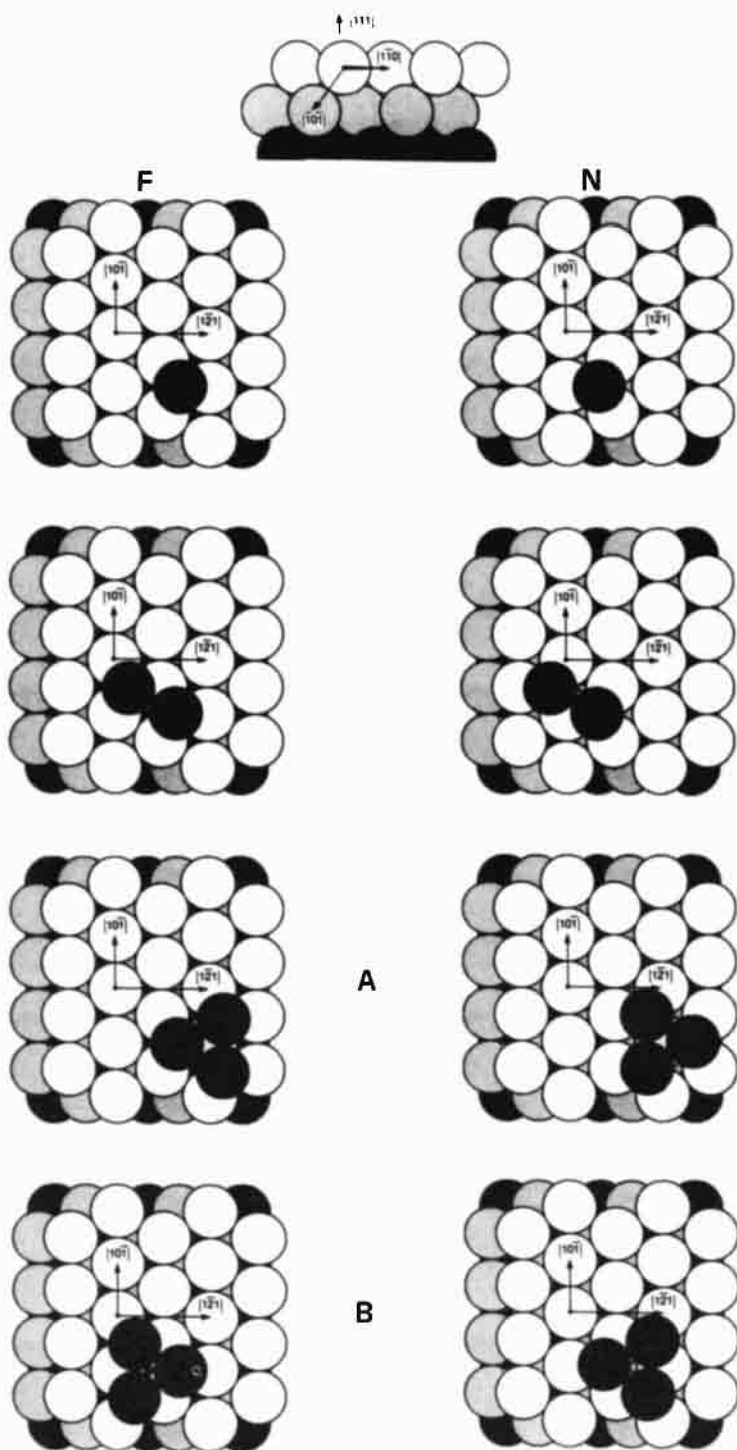


**Figure 4.** Possible atomic configurations for monomers, dimers and triangular trimers on (111) FCC surfaces at normal (N) and fault (F) sites. Trimers of type A have their center above an atom in the surface layer, for type B the center is at an adsorption site

continued fractions with 10 exact levels. Relaxation of the adatoms and their neighbours is taken into account in the following way : i) the adatom are allowed to relax perpendicularly towards the surface, ii) each adatom is assumed to give rise to an isotropic dilatation of their first nearest neighbours in the surface.

It is well known that in bulk crystals there are inversions of relative stability between the HCP and the FCC structure as a function of the d band filling which follow from the equality of the first four moments ( $\mu_0 - \mu_3$ ) of the total density of states in both structures<sup>3</sup>. A similar behaviour is also expected in the present problem since the total densities of states of two adislands with the same shape and number of atoms, but adsorbed in different geometries, have again the same  $\mu_0, \mu_1, \mu_2, \mu_3$  when the renormalization of atomic levels and the relaxation are neglected. This behaviour is still found when the latter effects are taken into account as shown in Fig. 5 where our results are summarized.

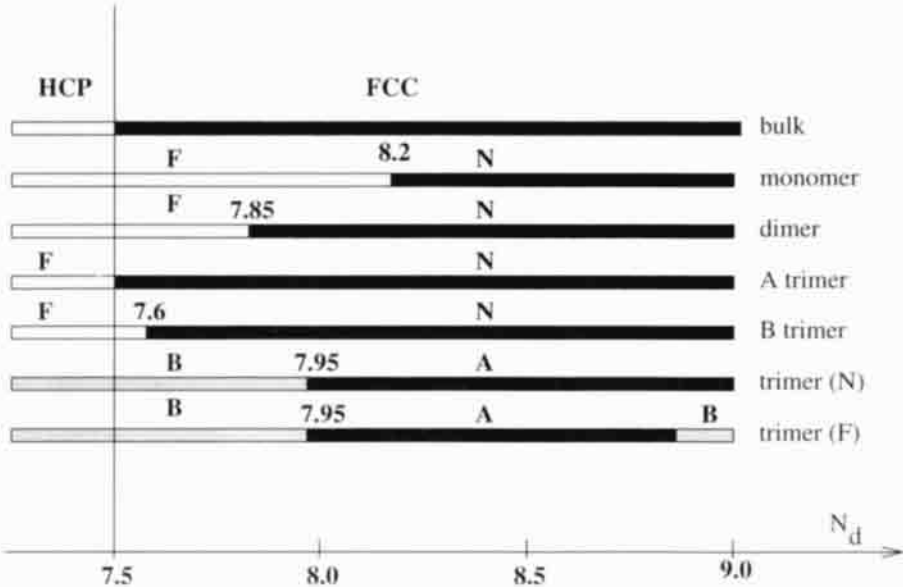


**Figure 5.** Diagram giving the relative stability of the various atomic configurations shown in Fig. 4 as a function of the d band-filling  $N_d$ . From the second to the fifth line : relative stability of the F and N sites for the monomer, dimer, A trimer and B trimer. On the sixth and seventh lines : relative stability of A and B triangles at N and F sites. The relative stability of HCP and FCC bulk phases is given for comparison in the first line.

It is seen that there exists a domain of d band-fillings  $N_d \in [7.5, 8.2]$  for which the HCP site is more stable than the FCC site for one adatom on a FCC (111) surface of the same chemical species. This domain narrows very rapidly when the cluster size increases. Consequently, outside this domain and in the range of stability of bulk FCC, i.e., when  $N_d > 8.2e^-/\text{atom}$ , we predict that cluster adatoms sit always at normal sites irrespective of the size of the



cluster. On the contrary for  $N_d \in [7.5, 8.2]$  a transition from fault to normal site is expected for clusters containing 2 or 3 atoms. Taking  $N_d \sim 7.5 - 7.6e^-/\text{atom}$  for Ir, we find, in accordance with experiments, that Ir monomers and dimers occupy fault sites, whereas fault and normal triangular trimers have almost the same adsorption energy but B triangles are significantly more stable than A triangles. If we note that Rh has the FCC structure and that its band-filling must be close to that of Ir since they belong to the same column in the periodic table, we predict the same kind of behaviour for this element. It would be interesting to have experiments performed on this metal. Predictions for Pd and Pt would be risky since in these metals, the effect of sp electrons is not negligible.

It should be noted that relaxation effects play an important role on these results. Indeed it is found that, especially for monomers by also for dimers, the relaxation is larger at fault sites than at normal sites when  $N_d \lesssim 8e^-/\text{atom}$  while the opposite occurs for  $N_d \gtrsim 8e^-/\text{atom}$ . This tends to increase the range of stability of the fault site. It must be emphasized that second moment calculations (13) cannot account for this effect since they are quite insensitive to lateral relaxations. Actually, in such relaxation some distances are expanded whereas some others are compressed and the net effect on the second moment nearly cancels.

## CONCLUSION

We have shown that a tight-binding scheme accounts for many physical phenomena which are of importance for the understanding of the energetics of surface defects and of crystal growth. This method which is simple and much less computer time demanding than ab initio methods is thus very useful to derive trends along the transition series.

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# STACKING FAULT ENERGIES IN AL-BASED ALLOYS

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## INTRODUCTION

Al-based alloys such as Al-Cu and Al-Mg have interesting superplastic properties which are usually assigned to sliding at grain boundaries. Even though the underlying mechanisms of superplastic behavior and grain boundary sliding are not understood at an atomic scale, some empirical relations between structural and superplastic properties are known. Among them is the observation, that grain boundary sliding and therefore superplasticity are favored in alloys with small grains that have wide grain boundary regions.

Some established connections between stacking faults and mechanical properties should be mentioned, in order to clarify the purpose of a detailed study of stacking fault energies (SFE) in alloys. At a mesoscopic scale, an important physical process that is involved during the deformation of materials is the emittance and interaction of dislocations. In face centered cubic (fcc) metals dislocations release energy by splitting into partials, where the equilibrium distance between these partials is determined by the energy of the intrinsic stacking fault, which is formed between them. The conventional view [1] is, that when the SFE is high, such as in Al, cross-slip of dislocations is easy so that annealing of deformation-induced defects occurs by dynamic recovery of the grains. On the other hand, when the SFE is low, the material recrystallizes dynamically during hot deformation. On an atomistic scale, the SFE, or more generally, energy differences between simple structures, are known to be closely related to the atomic structure at grain boundaries [2]. Obviously, the grain boundary structure has to be known, in order to understand at an atomic scale the physical mechanism that underlies the role of grain boundaries during the superplastic deformation of metals. Inter-atomic potentials, which form the crucial input to large scale atomistic computer simulations of material properties, have to be designed to reproduce basic quantities such as the SFE. The investigation of grain boundaries and their influence on the mechanical properties in alloys is complicated by the fact, that the composition at the boundary is not homogeneous and often very different from

the average composition of the material due to segregation. Basic physical quantities can show a strong composition dependence which can not be predicted from their magnitudes for the pure constituents of the alloy. For example the SFE decreases rapidly when Al is alloyed to Cu [3], even though the SFE in pure Al is much larger than in pure Cu. Since most of the Al-based alloys have a strong tendency towards phase separation, it is not possible to assess the SFE and other basic quantities from experiments at compositions that reflect the local chemical environment of an atom at the grain boundary.

From a theoretical point of view, stacking fault energies in metals have been reliably calculated from first-principles with different electronic structure methods [4, 5, 6]. For random alloys, the Layer Korringa Kohn Rostoker method in combination with the coherent potential approximation [7] (LKRR-CPA), was shown to be reliable in the prediction of SFE in fcc-based solid solution [8, 9].

In this work, we present calculated SFE using the LKRR-CPA method for Al-Cu and Al-Mg which are of interest from the point of view of superplasticity. We use the SFE to validate the rigid band model which allows a deeper insight into the electronic structure and its implication on the nature of inter-atomic potentials.

## RESULTS

In all calculations reported here, the close packed solid is described as a superposition of (111) layers. The CPA is applied to this geometry using the LKRR multiple scattering approach [7] with all layers having the same average composition. The atomic sphere approximation is assumed where all atoms are taken to have equal radii [10]. In the stacking fault calculations, eight (111) layers with a ABCACABC stacking sequence were embedded self-consistently in a fcc crystal which has the usual ...ABCABC... stacking sequence. The procedure allows the electronic structure to relax in four layers on each side of the intrinsic stacking fault. The SFE is calculated from the difference in total energies between these eight layers with stacking fault and eight layers of the undisturbed fcc crystal. We have also calculated total energies for the ...ABABAB... stacking sequence, which defines the hexagonal closed packed (hcp) structure.

Figure 1 summarizes the results of stacking fault calculations for solid solution Al-Cu and Al-Mg. Upon addition of Al to Cu, the SFE decreases, as is known from previous experimental and theoretical work [3, 8]. On the Al-rich side, the fault energy increases when Cu is added. Note that this does not reflect the observation, that the superplastic properties of Al improves, when Cu is added. An increasing SFE would lead to sharper grain boundaries and therefore reduce the possibility of grain boundary sliding. However, it must be noted, that since Al-Cu shows a strong tendency towards phase separation, the alloy composition at the grain boundary is expected to be Cu-rich, for which the SFE is close to zero.

In the Al-Mg system the compositional dependence of the SFE is almost a straightforward interpolation between the fault energies of the pure elements, i.e. the SFE decreases upon addition of Mg to Al, a finding that is confirmed experimentally [11].

Rosengaard and Skriver [5] have demonstrated, that in all 3d, 4d, and 5d transition metals, the intrinsic stacking fault energy,  $\gamma$ , can be accurately estimated from the relation,

$$\gamma = 2(E(hcp) - E(fcc)). \quad (1)$$

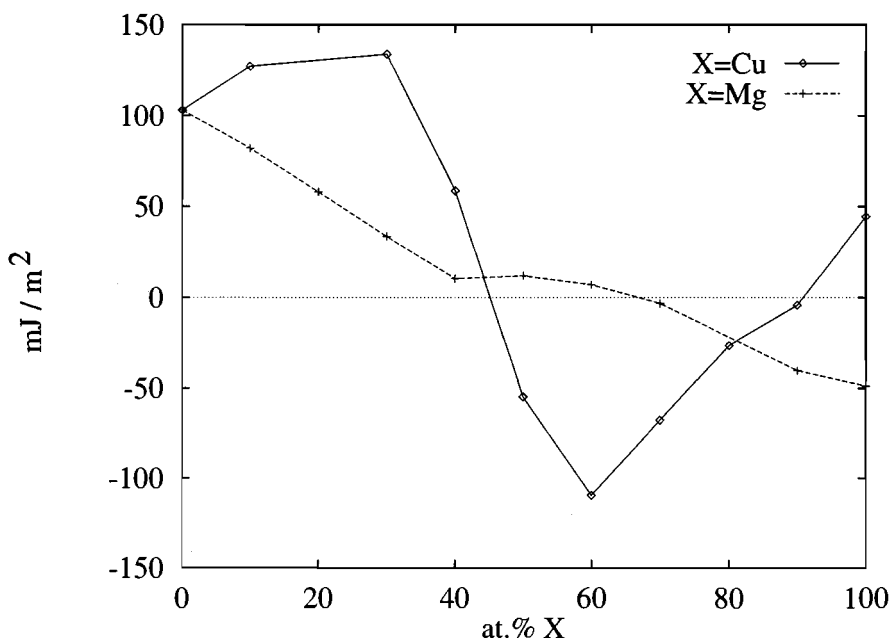


Figure 1: Intrinsic stacking fault energy for chemically disordered solid solution Al-X (where X=Cu or Mg) as a function of composition.

As we show in Fig. 2 this relation holds as well for the two Al-based alloys studied here. This finding has consequences on the nature of the inter-atomic interactions. From a fcc point of view, the hcp structure has a stacking fault every second layer. The fact that relation (1) holds means that these stacking faults weakly interact, and therefore the range of the inter-atomic interactions should not go beyond the second neighbor shell whereas conventional central potentials require at least three atomic shells to differentiate the fcc and hcp stacking sequences.

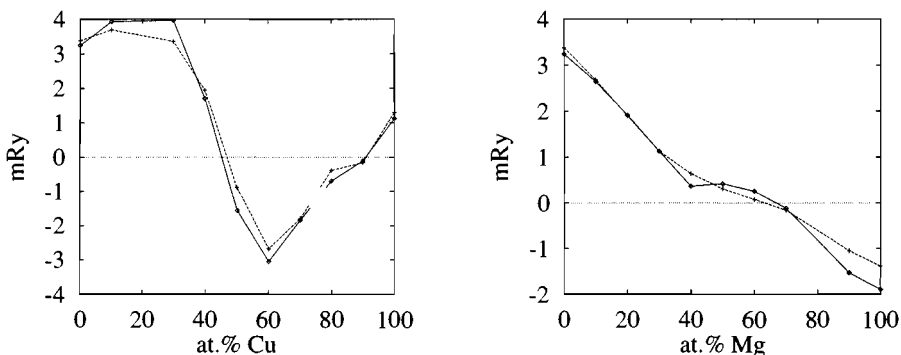


Figure 2: Comparison between intrinsic stacking fault energy (solid line) with two times the energy difference between the hcp and the fcc structure (dashed line) for Al-Cu (left panel) and Al-Mg (right panel) solid solution as a function of alloy composition.

# RIGID BAND MODEL

The SFE, which we have determined from fully self-consistent calculations, can also be found to good accuracy from non-self-consistent calculations, in which a bulk potential is used in a “single shot” fault-calculation [4]. Using the force theorem, the SFE is calculated from the difference in band energy between the fault geometry and the perfect crystal, and a correction for the extra charge accumulated in the stacking fault region [8]. The decrease in the SFE when Al is added to Cu has been explained by an even simpler rigid-band approach [8], in which the band energy is calculated from the density of states (DOS) of Cu only, after the Fermi energy has been adjusted to give the correct number of valence electrons at a given concentration of Al.

We will now show, that a slightly modified rigid band approach can reproduce the compositional dependence of the SFE in Al alloyed with Cu at all compositions. Starting with the DOS,  $n^{Al}(E)$  and  $n^{Cu}(E)$ , of the pure elements, we adjust the Fermi energies  $E_f^\alpha(c)$  for each composition of the alloy  $Al_{(1-c)}Cu_c$  such that

$$\int_{-\infty}^{E_f^\alpha(c)} n^\alpha(E) dE = Z^\alpha - Z_{\text{core}}^\alpha + dq^\alpha(c). \tag{2}$$

where  $Z^\alpha$  and  $Z_{\text{core}}^\alpha$  are the atomic number and the number of core electrons, respectively. The term  $dq^\alpha(c) = c_\alpha(N^\beta - N^\alpha)$  accounts for the correction in the valence from the second constituent  $\beta$  of the alloy.  $N^{Al} = 3$  and, since the  $d$ -band in Cu is filled at all compositions,  $N^{Cu} = 1$ . Assuming that the charge transfer between the species is negligible we can choose the zero of energy for each component,  $\alpha$ , such that  $E_f^\alpha(c) = 0$ , and then combine the two DOS's according to  $n_c^{\text{Alloy}}(E) = n^A(E)(1 - c) + n^B(E)c$ , from which the band energy can be calculated by

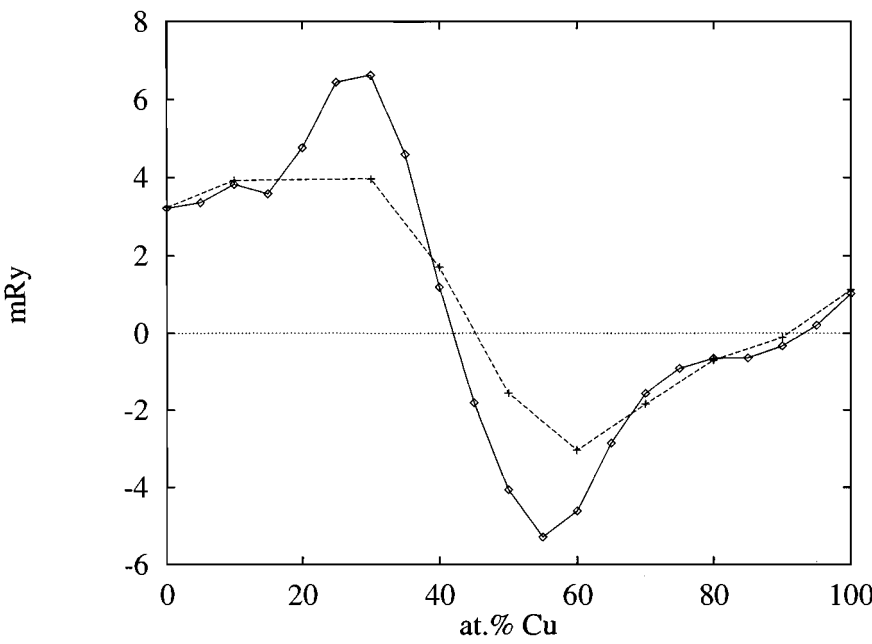


Figure 3: Compositional dependence of the stacking fault energy calculated from the rigid-band model (solid line) compared with the more accurate results from the LKKR-CPA calculation (dashed line) for the Al-Cu alloy system.

integrating from  $-\infty$  to 0. Finally the SFE is calculated from the difference in band energies.

The rigid band model reproduces the compositional dependence of the SFE very well, as is shown in Fig. 3 for the Al-Cu system. Similar agreement is obtained for the energy difference between the hcp and fcc structures. We can thus conclude, that the variation of the structural energy difference is mainly due to the population of *sp*-states close to the Fermi energy of, respectively, the noble metal and Al. The contribution of the *d*-states of Cu to this structural energy difference is constant. The SFE and the energy difference between hcp and fcc structures not only depend on the width of the occupied band but also on the details of the structure of the DOS at the Fermi energy. When translated into a moment expansion of the DOS we can conclude, that the second moment which relates to the width of the DOS, does not suffice to describe the compositional dependence of these energy differences. Higher order moments and thus many-body interactions are required to properly describe the structural energy variation with composition in Al-base alloys, and Al-Cu in particular.

## SUMMARY

We have calculated the intrinsic stacking fault energy in Al-Cu and Al-Mg. While compositional variation of the SFE in Al-Mg is almost a straight forward interpolation between fault energies of pure elements, it has a strongly non-linear dependence in the case of Al-Cu, which can be understood in the framework of a rigid band model. In both alloy systems the SFE compares well with twice the energy difference between the hcp and the fcc structures. Our results indicate that the inter-atomic interactions that lead to a correct description of the compositional dependence of the SFE are limited to the first two neighbor shells and include clusters with more than two atoms.

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## CHEMICAL BONDING AND ELASTIC CONSTANTS OF NICKEL-BASED INTERMETALLICS

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### INTRODUCTION

The  $L1_2$ -type ordered nickel-based intermetallic series,  $Ni_3X$  ( $X = Mn, Al, Ga, Si, Ge$ ), provide a class of systems exhibiting unique mechanical properties that make them attractive for structural applications at elevated temperatures.<sup>1</sup> One of the outstanding features of plastic deformation in this class of systems is the anomalous increase in flow stress with increasing temperature in contrast to conventional compounds.<sup>2</sup> Their resistance to oxidation, the low density and the high melting temperatures are also of central interest. To interpret the anomalous yield behavior of  $L1_2$  alloys, Yoo<sup>3</sup> proposed that the effect of *elastic anisotropy* on the temperature dependence of yield stress is as important as the anisotropy of antiphase boundary energy<sup>4</sup> in describing dynamic breakaway of superpartial screw dislocations from cross-slipped segments.<sup>5</sup> Recent measurements<sup>6</sup> of single crystal elastic constants for this series of Ni-based type compounds indicate a large elastic anisotropy factor,  $A$ , ranging from 2.5 to 3.3, except for  $Ni_3Ge$  ( $A = 1.72$ ). An inherent drawback to using this class of intermetallics as useful structural materials is the tendency of polycrystalline ordered stoichiometric alloys (except for polycrystalline  $Ni_3Mn$ ) to undergo brittle intergranular fracture, even though single crystals of  $Ni_3X$  are highly ductile.<sup>1</sup> The available experimental data indicate a strong effect of chemistry on the tendency for brittle intergranular fracture, with the resistance to fracture increasing in the order  $X = Ge < Si < Ga \sim Al < Mn$ .<sup>7</sup> The trend of intergranular fracture behavior in polycrystalline  $Ni_3X$  (grain-boundary cohesive strength) has been found to correlate well with the difference in atomic electronegativity,<sup>7</sup> the difference in valency,<sup>8</sup> and the relative  $s$ -orbital electronegativities<sup>9</sup> of the atomic constituents of the compound.

In this paper we report first principles total energy electronic structure calculations of the elastic constants of the  $L1_2$ -type ordered nickel-based intermetallic series,  $Ni_3X$ ,  $X = Mn, Al, Ga, Si, Ge$ . The elastic constants contain some of the most important information that can be obtained from ground-state total-energy calculations. The elastic constants determine the response of the crystal to external forces, as characterized by the bulk modulus, shear modulus, Young's modulus, and Poisson's ratio, and so play an important part in determining the strength of a material. There is also a tendency toward correlation between the elastic constants and the melting temperature of a solid.<sup>10</sup> In addition to being the most fundamental mechanical properties, the elastic constants provide basic information about the nature of interatomic interactions in solids. The purpose of this work is to investigate the origins in the electronic structure of the variation of the elastic constants with chemical environment across the series, to examine whether the ratio of bulk modulus to shear modulus  $\frac{B}{G}$  (a parameter associated with the deformation ability of a compound<sup>11</sup>) correlates with the difference in electronegativity,<sup>7</sup> and to understand the nature of the chemical bonds responsible for the unusual mechanical behavior of this class of systems. From an electronic structural point of view, the difference on going from  $Ni_3Al$  to  $Ni_3Si$  and from  $Ni_3Ga$  to  $Ni_3Ge$  is the addition of an extra  $p$ -electron on the  $X$  atom.

In crystals with the  $L1_2$  structure (the fcc-based ordered structure), there exist three independent elastic constants in the contracted notation,  $C_{11}$ ,  $C_{12}$  and  $C_{44}$ .<sup>12</sup> A set of three independent *ab initio* total-energy calculations (i.e. total energy as a function of strain) is required to determine these elastic constants. We have determined the bulk modulus,  $C_{11}$ , and  $C_{44}$  from distortion energies associated with uniform hydrostatic pressure, uniaxial strain and pure shear strain, respectively. The shear moduli for the  $\{001\}$  plane along the  $[100]$  direction and for the  $\{110\}$  plane along the  $[1\bar{1}0]$  direction, are  $G_{\{001\}} = C_{44}$  and  $G_{\{110\}} = \frac{1}{2}(C_{11} - C_{12})$ , respectively. The shear anisotropy factor,  $A = \frac{2C_{44}}{(C_{11} - C_{12})}$ , provides a measure of the degree of anisotropy of the electronic charge distribution.

The total energy has been calculated by means of self-consistent first-principles electronic structure calculations based on the full-potential linear-muffin-tin-orbital (FLMTO) method.<sup>13</sup> Because the atomic bonding in intermetallics has both metallic and directional characteristics, a full potential approach is essential. The calculation for the determination of elastic constants is far more sophisticated than the calculation of bulk properties (i.e., lattice constants, heat of formations, etc.). The elastic constants are evaluated at the theoretical equilibrium volume. The application of strain on the lattice implies a lowering of symmetry from that of the bulk crystal and the strain energy involved is small, typically of the order 0.01 eV/atom or less for a 1% strain. Therefore, very accurate total energy calculations are required. The  $k$ -point sampling was done using the "special-point" method.<sup>14</sup> The number of  $k$  points was increased until the total energy was converged to less than  $\sim 0.1$  mRy. The bulk modulus was calculated using 84  $k$ -points in the irreducible wedge of the cubic Brillouin zone; the calculations of  $C_{11}$  and  $C_{44}$ , which involve a lowering of the symmetry, were carried out with 126 and 125  $k$ -points, respectively. Two sets of tail parameters  $\kappa$  (the kinetic energy of the bases in the interstitial) were used, one floating at the average interstitial kinetic energy and the other, set fixed at an optimized value for the energy of a particular state (for example of the semi-core  $3d$  state of gallium). This method of choosing the various tail parameters has been found in a number of tests to reliably give those values which minimize the total energy. We have found that varying  $\kappa^2$  by 0.1 Ry results in changes of the total energy from 2 to 15 mRy.

## NUMERICAL RESULTS AND DISCUSSION

The calculated and experimental<sup>6</sup> values of the equilibrium lattice constant, bulk modulus and elastic stiffness constants across the Ni<sub>3</sub>X series are listed in Table I. With the exception of Ni<sub>3</sub>Ga, the calculated values of the elastic constants agree with the experimental values to within 30 %. The calculated elastic constants of Ni<sub>3</sub>Ga show a large discrepancy with the experimental values. Our calculated value of  $2.49 \times 10^{11} \frac{\text{N}}{\text{m}^2}$  for the bulk modulus for Ni<sub>3</sub>Ga, which agrees well with the FLAPW result of  $2.24 \times 10^{11} \frac{\text{N}}{\text{m}^2}$ ,<sup>15</sup> differs substantially from experiment. The error in  $C_{44}$  of Ni<sub>3</sub>Ge is also large; using the experimental values of the lattice constant instead, we find that  $C_{44} = 1.49 \times 10^{11} \frac{\text{N}}{\text{m}^2}$  and  $C_{11} = 3.32 \times 10^{11} \frac{\text{N}}{\text{m}^2}$ , in better agreement with experiment. Also listed in Table I are values of the shear moduli  $G_{\{001\}} = C_{44}$  and  $G_{\{110\}} = \frac{1}{2}(C_{11} - C_{12})$ , the anisotropy factor A, and the Poisson's ratio  $\nu$ , respectively. The larger values for  $G_{\{001\}}$  compared to those for  $G_{\{110\}}$ , suggest that these compounds shear easier on the  $\{110\}$  rather than on the  $\{001\}$  planes. Furthermore, the shear moduli increase on going from Ni<sub>3</sub>Mn to Ni<sub>3</sub>Si. It has been suggested<sup>18</sup> that the large values of A can give rise to the driving force (i.e., tangential forces) acting on screw dislocations to promote the cross-slip pinning processes.

Many of the intermetallic alloys are not available as single crystals, but the isotropic bulk and shear moduli can be measured from polycrystalline samples. Using our calculated elastic constants for single crystals, we have calculated the shear modulus G, and the Young's modulus E for polycrystalline systems using the Hill's method.<sup>19</sup> Table I presents these results, including the experimental measurements<sup>6</sup> when they are available. The ratio,  $\frac{B}{G}$ , has been suggested to provide an indication of the deformation ability.<sup>11</sup> The resistance to plastic deformation is proportional to G and the burgers vector, b, while the fracture strength is proportional to the bulk modulus, B, and the lattice constant. The higher the value of  $\frac{B}{G}$ , the more ductile the material would be. Although the attribution of the extent of fracture range solely to the  $\frac{B}{G}$  ratio is highly simplistic, it nevertheless indicates the tendency of brittleness for the Ni<sub>3</sub>X intermetallics. Interestingly, the  $\frac{B}{G}$  ratio is found to decrease on going from Ni<sub>3</sub>Mn to Ni<sub>3</sub>Si, suggesting a corresponding decrease of ductility. This trend of the  $\frac{B}{G}$  ratio is similar to the trend of the tendency for brittle intergranular fracture, with the grain-boundary cohesive strength changing in the order Ni<sub>3</sub>Mn > Ni<sub>3</sub>Al > Ni<sub>3</sub>Ga > Ni<sub>3</sub>Si.<sup>7</sup> We find that the  $\frac{B}{G}$  ratio decreases linearly with the difference in atomic electronegativity between Ni and X as suggested by Taub *et al.*<sup>7</sup>

The mechanical strength of materials is due ultimately to the atomic bonding strength. The shearing in a certain direction involves the stretching of bonds and termination of the elastic regime involves the breaking of bonds. To gain an understanding of the changes of bonding characteristics on going from Ni<sub>3</sub>Al to Ni<sub>3</sub>Si, we present in Fig. 1(a) the bonding-charge-density contour plots on the (001) plane (i.e. a mixed Ni-X, X = Al, Si plane). The bonding charge density, is defined as the difference of the total charge density in the solid and the superpositions of neutral atomic charge densities placed at atomic sites, i.e.,  $\Delta\rho(\mathbf{r}) = \rho_{\text{solid}}(\mathbf{r}) - \sum_{\alpha} \rho_{\alpha}(\mathbf{r} - \mathbf{r}_{\alpha})$ . The bonding charge density represents the net charge redistribution as atoms are brought together to form the crystal. The solid and dotted curves represent accumulation (depletion) of electronic charge. For all compounds, we observe a depletion of charge from the X sites and a build-up of directional d-bonding charge at the Ni sites. In both compounds we find that the depletion of electron density at the X(Al or Si) sites is accompanied by significant *anisotropic* buildup of the directional d-bonding charge at the nickel sites along the nearest neighbor Ni-X direction. The bonding directionality is caused mainly

**Table I.** Experimental and calculated lattice constants  $a$  (in Å), elastic constants, bulk and shear moduli (in units of  $10^{11} \frac{N}{m^2}$ ) for the  $Ni_3X$  ( $X = Mn, Al, Ga, Ge, Si$ ) intermetallic series. Also listed are values of the anisotropy factor  $A$  and Poisson's ratio  $\nu$ . The experimental data for  $a$  are from Ref.<sup>16</sup>. The experimental data for  $B$ , the elastic constants,  $A$  and  $\nu$  are taken from Ref.<sup>6</sup>. The theoretical values for  $Ni_3Si$  are from Ref.<sup>17</sup>. Also listed in the table are values of the polycrystalline elastic quantities-shear moduli  $G$ , Young moduli (in units of  $\frac{N}{m^2}$ ) and the ratio  $\frac{B}{G}$ . The experimental data for these quantities are from Ref.<sup>6</sup>

| Comp.    | $a$       | $B$  | $C_{11}$ | $C_{12}$ | $C_{44}$      | $G_{\{110\}}$ | $A$  | $\nu$ | $G$  | $\frac{B}{G}$ | $E$  |
|----------|-----------|------|----------|----------|---------------|---------------|------|-------|------|---------------|------|
|          |           |      |          |          | $G_{\{001\}}$ |               |      |       |      |               |      |
| $Ni_3Mn$ | 3.44      | 2.70 | 3.18     | 2.46     | 1.64          | 0.36          | 4.56 | 0.436 | 0.90 | 2.99          | 2.44 |
|          | exp. 3.59 | 1.92 | 2.45     | 1.65     | 1.45          | 0.40          | 3.66 | 0.403 | 0.75 | 2.26          | 2.55 |
| $Ni_3Al$ | 3.48      | 2.34 | 2.78     | 2.12     | 1.86          | 0.33          | 5.64 | 0.433 | 0.95 | 2.46          | 2.51 |
|          | exp. 3.56 | 1.71 | 2.21     | 1.46     | 1.24          | 0.38          | 3.31 | 0.398 | 0.77 | 2.22          | 2.00 |
| $Ni_3Ga$ | 3.47      | 2.49 | 2.96     | 2.26     | 2.02          | 0.35          | 5.73 | 0.432 | 1.03 | 2.42          | 2.70 |
|          | exp. 3.58 | 1.46 | 1.91     | 1.23     | 1.08          | 0.34          | 3.17 | 0.392 | 0.68 | 2.16          | 1.76 |
| $Ni_3Ge$ | 3.49      | 2.42 | 3.26     | 2.00     | 1.90          | 0.63          | 3.02 | 0.380 | 1.22 | 1.98          | 3.14 |
|          | exp. 3.56 | 1.83 | 2.63     | 1.43     | 1.03          | 0.60          | 1.72 | 0.352 | 0.83 | 2.20          | 2.17 |
| $Ni_3Si$ | 3.43      | 2.57 | 3.47     | 2.12     | 2.24          | 0.68          | 3.32 | 0.379 | 1.39 | 1.85          | 3.53 |
|          | th. 3.46  | 2.60 | 3.75     | 2.00     | 1.67          | 0.88          | 1.91 | 0.351 | 1.29 | 2.02          | 3.32 |

by the polarization of the  $p$  electrons at the X sites as a result of the  $p$ - $d$  hybridization. On the other hand, while in  $Ni_3Al$  there is a significant buildup of interstitial bonding charge at the octahedral sites (sites between the next-nearest-neighbor (NNN) Ni and X sites), in  $Ni_3Si$  there is a depletion of bonding charge at the corresponding sites. The more pronounced directional bonding between the Ni and Si atoms, compared to that between the Ni and Al atoms, is responsible for the stronger resistance to shear in  $Ni_3Si$ , as indicated by the larger values of shear moduli of  $Ni_3Si$ . The bonding charge densities of  $Ni_3Ga$  and  $Ni_3Ge$  resemble those of  $Ni_3Al$  and  $Ni_3Si$ , respectively. Comparing the  $l$ - and site- projected density of states, we find that the addition of the  $p$  electron on going from Al to Si results in the lowering of the  $p$ -band with respect to the fermi energy and the filling of the Ni- $d$  hole. This results to a reduction of the density of states at the Fermi energy in  $Ni_3Si$ . In order to gain insight at the microscopic level into the redistribution of bonding charge as the systems undergo deformation, we present in Fig. 1(b) the bonding charge density contour plots on the (001) plane under a 2% pure shear strain along the [100] direction, for (a)  $Ni_3Al$  and for (b)  $Ni_3Si$ . One can see that the response of bonding charge to deformation is quite different for the two systems. The bonding charge density is preserved and only slightly deformed in  $Ni_3Al$ , while it changes substantially in  $Ni_3Si$ , indicating a greater resistance to shear (larger value for  $C_{44}$ ) in  $Ni_3Si$ .

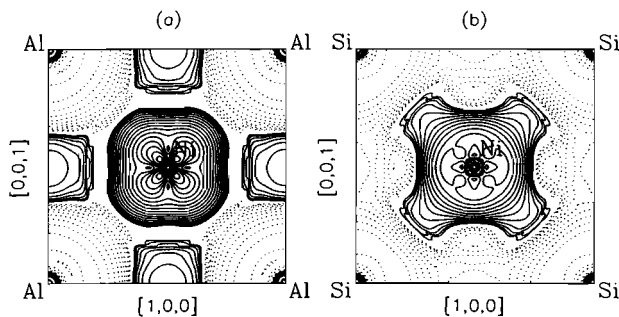


**Figure 1.** The charge-density difference (bonding charge density) between  $\text{Ni}_3\text{X}$  and the superposition of neutral Ni and X atomic charge densities on the (001) planes for (a)  $\text{X} = \text{Al}$  and (b)  $\text{X} = \text{Si}$ . The solid (dotted) contours denote contours of increased (decreased) density as atoms are brought together to form the  $\text{Ni}_3\text{X}$  ( $\text{X} = \text{Al}, \text{Si}$ ) crystal. Contours start from  $\pm 4.0 \times 10^{-4} e/(a.u.)^3$  and increase successively by a factor of root 2.

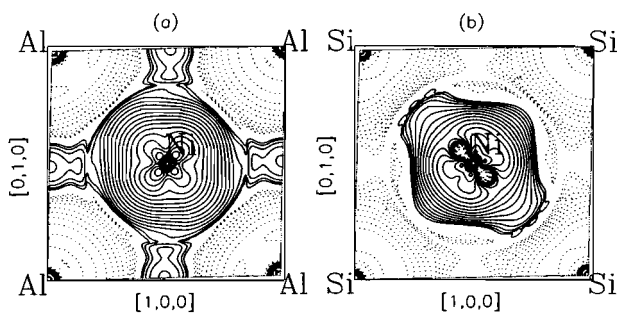


**Figure 2.** Bonding charge density on the (001) plane for (a)  $\text{Ni}_3\text{Al}$  and (b)  $\text{Ni}_3\text{Si}$  under a 2 % shear strain along the [100] direction. Contours start from  $\pm 4.0 \times 10^{-4} e/(a.u.)^3$  and increase successively by a factor of root 2.

To summarize, we have presented total-energy FLMTO electronic structure calculations of the elastic constants of the L1<sub>2</sub>-type ordered nickel-based intermetallics Ni<sub>3</sub>X (X= Mn, Al, Ga, Si, Ge). The agreement between theory and experiment for the elastic constants is relatively good (with a maximum error of about 30%) except for Ni<sub>3</sub>Ga. The larger error in Ni<sub>3</sub>Ga might be due to the sensitivity of the semi-core 3*d* state to the choice of the tail parameter. The large values of the anisotropic factor across the series is due to the anisotropic distribution of bonding charge. The calculated  $\frac{B}{G}$  ratio for the polycrystalline systems is found to correlate well with the difference in atomic electronegativity between Ni and X, as has been suggested experimentally.

## ACKNOWLEDGMENTS

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## THE MICROSTRUCTURE AND MARTENSITIC TRANSFORMATION IN A (POTENTIALLY) SHAPE MEMORY Ni-Al-Ti-B ALLOY

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### ABSTRACT

An alloy Ni-34.8at.% Al with addition of 0.5at.% of TiB<sub>2</sub> was investigated after homogenisation in the temperature range of the  $\beta$  phase and after hot deformation by 25 and 50%. The influence of microstructure on the martensitic transformation and fracture toughness was studied. The change of characteristic temperatures and temperature range of martensitic transformation as well as the increase of fracture toughness caused by the presence of the  $\gamma'$  phase were noticed.

### INTRODUCTION

The NiAl intermetallic compound after quenching from the temperature range of nonstoichiometric, high temperature  $\beta$  phase, undergoes thermoelastic martensitic transformation<sup>1</sup>. Many attempts to improve the poor ductility of NiAl by macro- and micro-alloying with third elements were undertaken. The research concerned mainly elements which stabilised the "soft"  $\gamma$  phase<sup>2</sup>. As Ti stabilises the  $\gamma'$  phase<sup>2</sup> it is not expected to improve the ductility of the  $\beta$  phase<sup>3</sup>, however it was shown that thin layer of the  $\gamma'$  phase at grain boundaries changed the fracture mode from intergranular to transgranular in Ni-AlFe and NiAlCo alloys<sup>4</sup>. It was also reported that a slip transfer occurred from the  $\gamma'$  to  $\beta$  phase in two phase NiAlTi alloy, deformed at room temperature<sup>5</sup>. Larger Ti contents suppress the martensitic transformation leading to the formation of metastable phases, not observed in NiAl alloys<sup>6</sup>. The influence of boron on the plasticity and fracture toughness of NiAl was widely studied. It was found that, in the case of stoichiometric alloys, ductility was not better, although the B addition altered the fracture mode<sup>7,8</sup>. The study of 2 wt% addition of TiB<sub>2</sub> suggested improvement of high temperature plasticity of NiAl alloys<sup>9</sup>.

The purpose of this paper was to study the influence of 0.5 at% of TiB<sub>2</sub> on pre-



cipitation of the  $\gamma'$  phase, the martensitic transformation and the fracture toughness of the Ni-Al alloy.

## EXPERIMENTAL PROCEDURE

The alloy was prepared from high purity Ni, Al and Al-5Ti-1B (wt.%) master alloy, by melting in a Balzers furnace under argon atmosphere and casting into a chill mould in vacuum. Samples after prolonged homogenisation at 1473 K ( $\beta$ -phase range), were plastically predeformed by hot upsetting in a "soft" carbon steel die at temperature 1273 K, and quickly cooled. Two degrees of deformation were applied, 25% and 50%. A part of the material deformed by 25% was rehomogenised at 1473 K.

The chemical composition of the alloy was carefully controlled after homogenisation and after hot upsetting, and it was : Ni - 34.8Al - 0.2Ti - B (at.%). As the boron content could not be detected, the nominal addition of 0.2 at.% was assumed.

## RESULTS

### The Microstructure of Homogenised and Hot Deformed Samples

The hot deformation process produced small grains which were elongated perpendicular to the compression axis, with a slightly differentiated average grain diameter, depending on the distance from the central part of the sample. In the rehomogenised sample the average grain size was 300  $\mu\text{m}$ , after 25% deformation grains were about 80  $\mu\text{m}$  big in the direction of the compression axis, and about 30% bigger in the perpendicular direction (Fig.1a). Unexpectedly, the sample after 50% deformation revealed large, partially recrystallised grains, elongated perpendicular to the compression axis, of average size about 10 times larger than in the sample deformed by 25%. In Fig.1b small subgrains at the boundaries of large grains and transgranular microcracks in the sample deformed 50% are visible. The electron microscopy examination of the matrix structure, showed the B2 structure with a long range atomic order. In the electron diffraction patterns strikes in  $\langle 110 \rangle$  and  $\langle 112 \rangle$  directions and satellites of the Bragg spots were usually present,

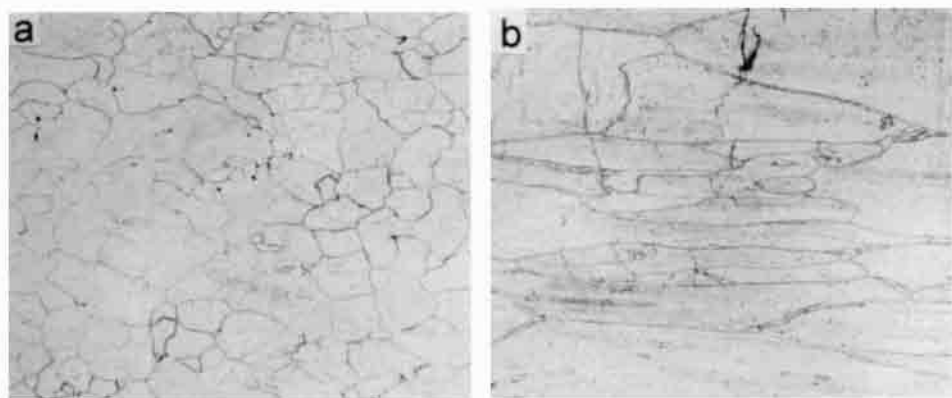


Fig.1. Optical microstructure of alloy after hot deformation: a) by 25 %, magnification 100x, b) by 50%, magnification 60x

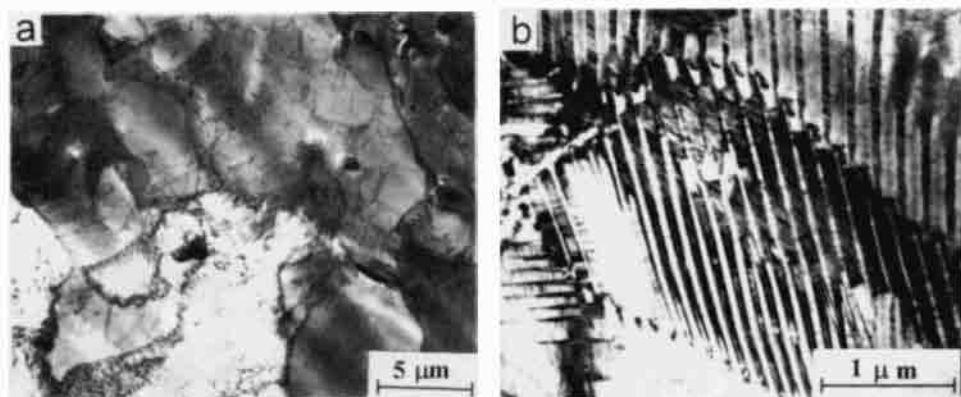


Fig.2. Electron microstructure of the sample hot deformed by 25% : a) matrix  $\beta$  phase, b) 7R martensite

which might be connected to small dilatation centres e.g. very small precipitates and/or premartensitic effects<sup>10</sup>. In the electron microstructure of the 25% deformed sample (Fig. 2a) small subgrains with a pronounced dislocation structure and the tweed type of contrast in the grains could be noticed. Different kinds of precipitates existed in both homogenised and hot deformed samples. Analysis of microcomposition showed that they could be divided in two groups: with high Ti content and with the composition of  $\text{AlNi}_6\text{Ti}$  ( $\gamma'$ ) phase. The Ti-rich precipitates were present in all samples and their amount was not affected by the hot deformation process. The  $\text{TiB}_2$  precipitates, of characteristic rectangular morphology, were noticed. The presence of  $\text{AlNi}_6\text{Ti}$  phase was induced mainly by the thermal and deformation processes after homogenisation in the  $\beta$  phase. In the sample after homogenisation, small amount of the  $\gamma'$  phase was located exclusively at some grain boundaries in the form of precipitates or of a thin, discontinuous film at the grain boundaries. Hot deformation process produced both, the continuous  $\gamma'$  phase at the grain boundaries and precipitates of lenticular shape within the grains (Fig.4). The 50% deformation introduced larger amount of such precipitates, distributed more regularly in the recrystallised grains.

### The Martensitic Transformation

The typical for Ni-Al alloys 7R and 3R ( $L1_0$ ) structures of martensite were formed in the investigated alloy. The thermally induced martensite in the homogenised sample was mainly of 7R type (Fig.2b). The  $L1_0$  martensitic structure was mainly observed in samples after the hot deformation.

The reversible, thermoelastic, martensitic transformation is strongly influenced by the matrix microstructure. Transformation hysteresis loops, obtained on the basis of calorimetric measurements, are presented in Fig.3. Curve 1 refers to the sample homogenised at 1473 K. Two-stage character of the transformation is clearly visible. Small grains and a high density of structural defects in the sample deformed by 25% (curve 2) resulted in lowering  $M_s$  and  $A_f$  temperatures but not  $M_f$  and  $A_s$ , decreasing strongly the temperature range of transformation - ( $A_f - M_f$ ). A short recrystallisation by continuous heating up to 773 K leads to the increase of the  $M_s$  and  $A_f$  temperatures by about 10 K (curve 3) and to decrease of the  $M_f - A_s$  difference. However, the main change in the microstructure, caused by this treatment, as was shown in the TEM study, was the additional precipita-

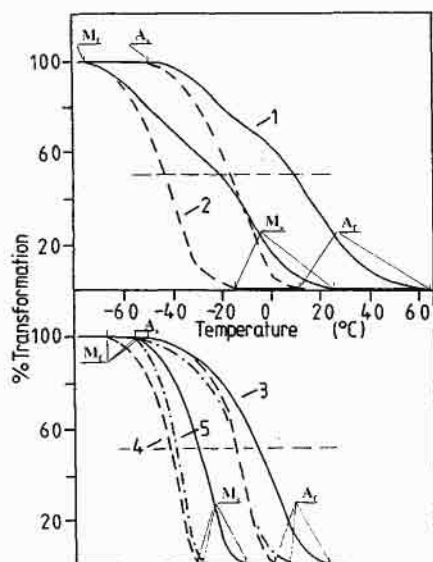


Fig.3. Martensitic transformation hysteresis loops, second cycle, heating rate 30 K/min.

tion of the  $\gamma'$  phase at 630 K. Ageing of 25% deformed sample for 8 hours (curve 4) and 16 hours (curve 5) at 510 K increased the slope of the loop and gradually decreased the difference in the  $M_r$  and  $A_s$  temperatures. As can be seen from the calorimetric curves, only after this ageing, the transformation completely lost its two stage character. The released energy of martensitic transformation, measured by the DSC was about 4J/g in each case. It should be noticed that the  $M_s$  temperature of the homogenised sample was lower by about 250 K than expected from the Ni/Al ratio<sup>11</sup>. This suggests a strong influence of Ti addition on lowering of the  $M_s$  temperature of the alloy. The  $M_s$  temperature of the sample hot deformed by 50%, after dynamic recrystallisation during this process, was about 4 K higher than that of the homogenised sample, supporting the opinion that the lowering of the  $M_s$  temperature of the sample deformed by 25% was mainly due to the structural defects introduced by the deformation process.

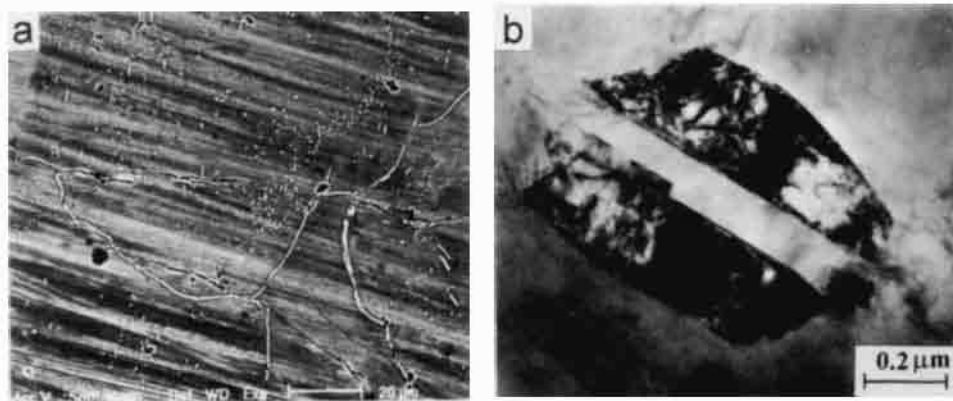


Fig.4. Sample hot deformed by 25% a) SEM microstructure after compression test at the room temperature and fracture, b) electron microstructure of the  $\gamma$  precipitate.

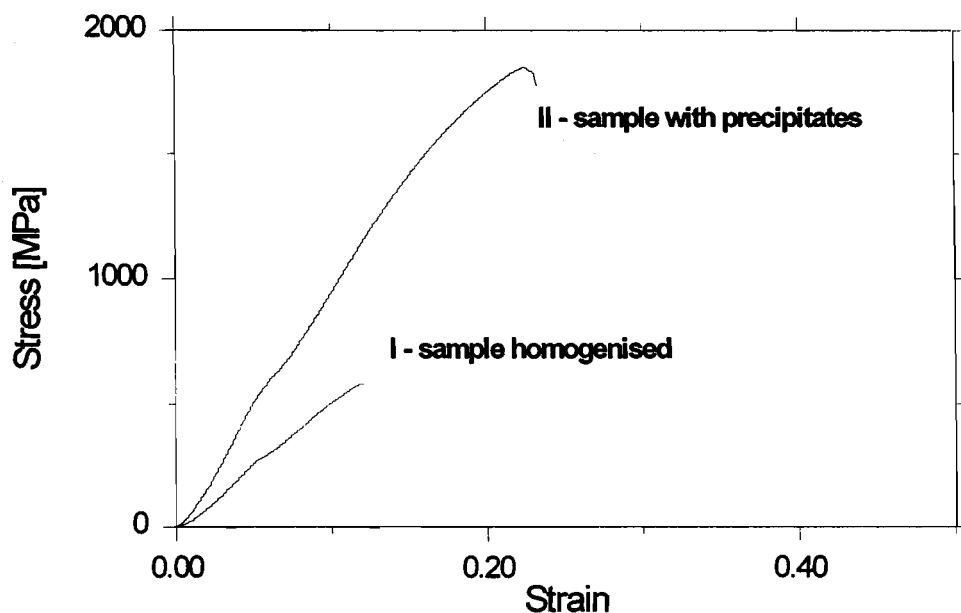


Fig.5. Stress-strain to fracture curves, ( $\epsilon = \Delta h/h_0$ )

### The Effect of Microstructure on the Deformation and Fracture

Two samples of the investigated alloy, homogenised and deformed by 25%, were submitted to the compression test at a rate 0.05 mm/min, at room temperature. The result presented in Fig.5 (elastic part of the strain in the figure was not subtracted) showed that the fracture toughness of the sample deformed by 25% was three times higher than for the same material which was homogenised. A small range of plastic deformation in that case is also visible. The optical and SEM observations carried out on prepolished surfaces of deformed samples revealed a different fracture mechanism. In the case of the homogenised sample, the fracture was generally intergranular when in the sample after hot deformation it was transgranular (Fig.4a). The examination of the grain boundaries proves that the layer of the  $\gamma'$  phase at the grain boundaries strengthens them and changes the fracture mode in the sample. Thin foils prepared from samples after deformation were examined by TEM. The experiment showed that under compression, the matrix phase transformed into the martensite. Three structures of deformation martensite were identified: 3R, 7R and 4R. Thus, strain-stress curves in Fig.5 present rather the effect of pseudoelasticity and fracture toughness of martensite than plasticity of the B2 matrix phase. The lenticular  $\gamma'$  precipitates in the volume of the hot-deformed sample were also observed by TEM. They remained unchanged when strained, except that dislocation structure or deformation twins formed under the straining (Fig.4b) accordingly to paper<sup>5</sup>.

### CONCLUSIONS

1. The small Ti addition, dissolved in the  $\beta$  phase of Ni- 34.8 at.% Al greatly lowered the  $M_s$  temperature.

2. The characteristic temperatures of the martensitic transformation, as well as the ( $A_f$  -  $M_s$ ) temperature range were strongly influenced by the microstructure of the alloy. Applied predeformation lowered both  $M_s$  and temperature range of transformation while the ageing at 510 K that followed decreased the width of the transformation.
3. The applied predeformation process promoted precipitation of the  $\gamma'$  ( $\text{AlNi}_6\text{Ti}$ ) phase in the form of thin layer at the grain boundaries or lenticular precipitates. The presence of the  $\gamma'$  phase as a layer at the grain boundaries changed the fracture mode from intergranular to transgranular, increasing fracture toughness at room temperature about three times. The lenticular precipitates of this phase also took part in the deformation process, accumulating internally the strain. No microcracks in precipitates or caused by their presence was observed.
4. The grain boundaries remained the weakest structural element in the alloy in absence of the continuous  $\gamma'$  phase at them, weaker than elements of martensite structure, while in the presence of  $\gamma'$  layer, the fracture occurred in martensite interfaces.

## Acknowledgement

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## TEXTURE AND STRUCTURE OF SUPERPLASTICALLY DEFORMED AlZn BASE ALLOYS

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### INTRODUCTION

Designers of new materials and research workers share deep interest in metals and alloys which reveal superplastic properties. The problems associated with the formation of superplastic state in metallic alloys are very interesting, considering not only the scientific aspects but particularly its suitability for industrial application. During superplastic deformation quite complicated shapes can be accomplished in just one operation and at much lower stresses than in an ordinary deformation process cutting costs and energy expenses. High elongations have been obtained in iron or cast iron in the range of temperatures corresponding to the  $\alpha$  -  $\gamma$  transformation<sup>1</sup>. The Al-Zn system investigated mainly by Russian authors, i.e. by Presnjakow<sup>2,3</sup> has also been found to be superplastic. Titanium alloys are known as the materials which have a very good ability to undergo superplastic deformation. The Ti6Al4V alloy after thermo- mechanical treatment deforms up to 2100 % elongation at 1123 K and at relatively high strain rate ( $\dot{\epsilon} = 1 \times 10^{-2} \text{s}^{-1}$ )<sup>4</sup>. The high strength of the alloys qualify them as the materials to produce complicated elements for aircraft industry. The superplastic deformation proceeds not only in the alloys which are considered as plastic but is also possible in others, known as totally undeformable. For instance, Ni - base intermetallic compounds have been investigated and deformed up to 391 % at 1273 K at relatively high strain rate ( $\dot{\epsilon} = 1 \times 10^{-2} \text{s}^{-1}$ )<sup>5</sup>. Also multicomponent nanocrystalline materials have high susceptibility for the superplastic deformation, and they can be deformed to very high elongations<sup>6</sup>. Recently many papers on the superplastic Al-Li alloys have appeared. Very fine, globular-like structure with grain size below 5  $\mu\text{m}$  is obtained after a complicated thermomechanical treatment and elongation of 1600% may be obtained<sup>7</sup>. Even composites of aluminium alloys reinforced by particles or whiskers can be superplastically deformed<sup>8</sup>.

Since the sixties' a lot has been done on the mechanism of superplastic deformation. Avery<sup>9</sup> explained superplasticity in terms of diffusional creep and dislocation climb motion. Cline and Alden<sup>10</sup> have suggested that grain boundary sliding is the most important mechanism at low strain rate and sufficiently high temperature, while at higher strain rate crystallographic slip becomes more important. Alden<sup>11</sup> has made an assumption that flow stress, elongation, strain rate sensitivity (SRS) parameter depend on strain rate, temperature of deformation and structure of the alloy (at the first approximation - grain size).

A ductile material can be stretched uniformly only when stable flow occurs. The stable flow of materials has been investigated by Hart<sup>12</sup>, who described the transition from the stable to unstable flow. The beginning of geometrical instability and localisation of strain is the limit of the stable flow. At temperatures above 0.5 T<sub>m</sub> (at equilibrium between recovery and hardening) the strain rate sensitivity parameter "m" may be derived from the expression:

$$\sigma = K \epsilon^N \dot{\epsilon}^m \tag{1}$$

where:  $\sigma$  - is flow stress, K - is constant,  $\epsilon$  - is strain and  $\dot{\epsilon}$  - is strain rate, m - is strain rate sensitivity parameter and N - is strain hardening parameter.

The strain rate sensitivity parameter depends strongly on temperature, grain size and strain rate. It rises with the increasing temperature of deformation and with decreasing grain size and strain rate. Generally, three deformation mechanisms are taken into consideration: grain boundary sliding (gbs), stress direction vacancy migration (diffusional mass transfer) and crystallographic slip with recrystallisation. Eventually, it was Packer<sup>13</sup> who proposed the relationship predicting the behaviour of the superplastically deformed metallic specimen within a very wide range of strain rates. The superplastic strain rate can be expressed in terms of an applied flow stress- $\sigma$ , temperature - T and activation energy of deformation - Q. Higashi<sup>14</sup> proposed the following expression:

$$\dot{\epsilon} = K (\sigma / E)^n (b/d)^p D_o \exp (-Q / RT) \tag{2}$$

where: E - is Young modulus, D<sub>o</sub> - is diffusion coefficient , R - is gas constant, d - is grain size, b - is Burgers vector, p - is grain size exponent and n is stress exponent.

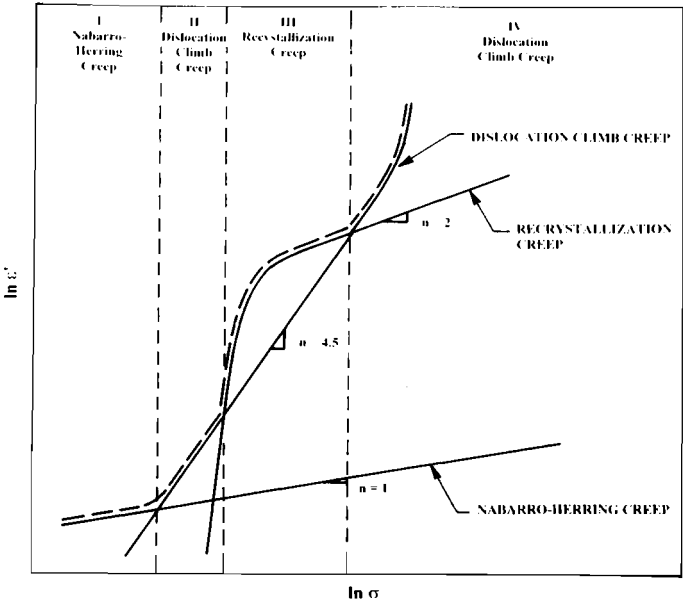


Fig.1. Prediction of the deformation behaviour of the material where three different processes may be rate and stress- controlled (dashed line)<sup>13</sup>.

The comparison of fractions of these mechanisms is possible only at comparable deformation conditions, for instance for the optimum strain rate (10<sup>-5</sup> - 10<sup>-3</sup> s<sup>-1</sup>). The share of the gbs mechanism depending on strain rate, grain size and shape has a maximum for the middle

range of strain rates and globular shape of grains. The contribution of the mechanism of diffusional mass transfer diminishes with the increase of strain rate and grain size within the middle range of the strain rates. This second statement results from Nabarro-Herring's and Coble's equations, according to which strain rate is inversely proportional to the square (N-H) or third power (Coble) of grain size. The share of crystallographic slip lowers very strongly with decrease of grain size and particularly with increase of temperature. That can be explained by higher flow stress of deformation at lower temperatures, while decrease of grain size leads to the increase of dislocation density.

According to Presnjakov<sup>2</sup> the best composition of the AlZn alloy, when the superplastic deformation is to be considered, is eutectoidal because the amounts of both phases ( $\alpha$  and  $\beta$ ) are equal, which is particularly advantageous for the grain boundary sliding to occur. In that case grain size (which should be of about 1  $\mu\text{m}$ ) and shape of the grains which should be equiaxed (globular), are very important. It has been stated that superplastic deformation does not only produce new texture types<sup>15, 16</sup> but also weakens the existing one, especially in the zinc phase<sup>17</sup>. Deformation at high strain rates (the third range) generates textures in both Al and Zn phases<sup>18</sup>. Within the second range of strain rates, dislocation slip is concentrated in external parts of grains (in Kornmantel) whose interior remains free of dislocations. Within the third range, dislocation nets and low-angle-boundaries appear in the whole grain. The results of works<sup>19, 20</sup> reveal that superplastic deformation leads to the formation of texture components, which are stable during the crystallographic slip. But, as Lee<sup>21</sup> has stated, the final texture in the sample deformed superplastically (at 533K and strain rate  $10^{-3}$ - $10^{-1} \text{ s}^{-1}$ ) was affected not only by the crystallographic slip but also by the strain induced recrystallisation and continuous recovery.

The aim of this study is to determine the structure and texture of the initial sample and the temperature and strain rate parameters, at which the superplastic deformation in AlZn78, AlZn76Cu2 and AlZn78 Mg0.02 alloys is the most likely to occur.

## EXPERIMENTAL PROCEDURE

The aluminium alloys AlZn78; AlZn76.5Cu1.5; AlZn76Cu2 and AlZn780.02Mg (all compositions in wt %) were continuously cast and extruded, then homogenised at 643K for 5 hours, quenched in room temperature water and aged at room temperature. Very fine, partially lamellar and globular two phase grain structure was obtained. Then, 48-hour annealing at 533K was applied to obtain a globular average structure (about 1 $\mu\text{m}$  in size). The structure investigations were performed by using of scanning microscopy with quantitative image analysis, TEM and texture X-ray diffraction techniques. The strength tests (tension and compression) were performed on the "INSTRON" testing machine in the temperature range from room temperature up to 573K and strain rates  $1 - 5 \times 10^{-3} \text{ s}^{-1}$ . The grain structure observations were carried out in the PHILIPS XL-30 scanning microscope. The TEM observations were carried out using the CM20 Philips transmission microscope. Thin foils were obtained by jet electropolishing in an electrolyte containing 33% $\text{HNO}_3$ , 67% $\text{CH}_3\text{OH}$  at  $-40^\circ\text{C}$ . The texture analysis of both Al and Zn phases was done based on two sets of incomplete pole figures (100), (110), (311) and (0001), (1011), (1012), respectively measured by means of the PHILIPS PW1710 diffractometer with X'Pert texture goniometer. The orientation distribution functions were calculated from the pole figures using the direct ADC method<sup>22</sup>.



RESULTS AND DISCUSSION

Scanning microscopy investigation and quantitative image analysis

The morphology of globular type is the most favourable when superplastic deformation is to occur in Al78wt%Zn alloy. This type of structure is formed by decomposition of the  $\alpha$  solid solution  $\alpha \rightarrow \alpha' + \beta$ <sup>2</sup>. However, plates usually dominate in the structure of this alloy. To obtain the non-plate or globular type, a special heat treatment is necessary i.e. the optimal cooling rate as well as the temperature and time of ageing.

The influence of cooling rate after homogenisation on type of structure was examined by the scanning electron microscope and quantitative image analysis. The alloy was cooled from 643K at rates ranging from 20 to 2000 K/s and subsequently aged at room temperature for 10 hours. It was stated that increase of cooling rate from 500 K/s and ageing at 293K caused a drop of amount of the plates.

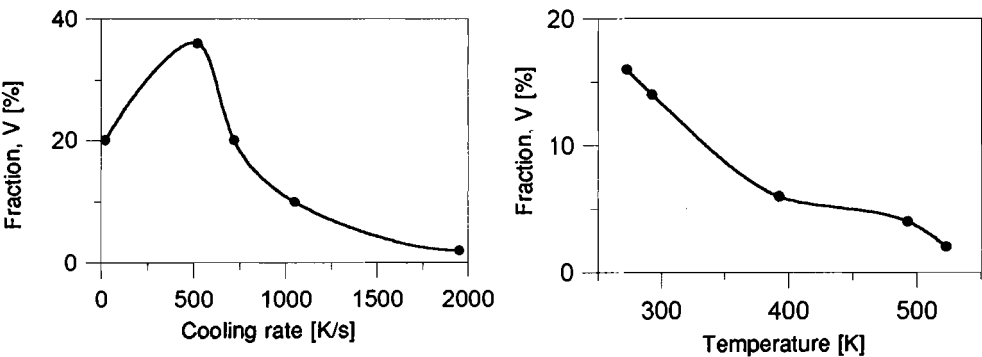


Fig. 2. Amount of the plate-like phases of AlZn78 alloy versus cooling rate (left) and ageing temperature for 10 hours (right).

The maximum amount of plates was 35% at 500 K/s (Fig.2) while at 1950 K/s the contribution of plates was 5% only. The remaining 95% of structure was covered with near globular forms.

The influence of ageing temperature on the alloy structure after cooling at 500 K/s rate from 643K to room temperature was examined at temperatures from 273 to 533K and is shown in Fig. 2 ( right). The temperature rise caused continuous diminishing of the amount of lamellar forms e.g. from 16% at 273 to 2% at 525K. The rest of the microstructure comprises irregular and partially globular forms.

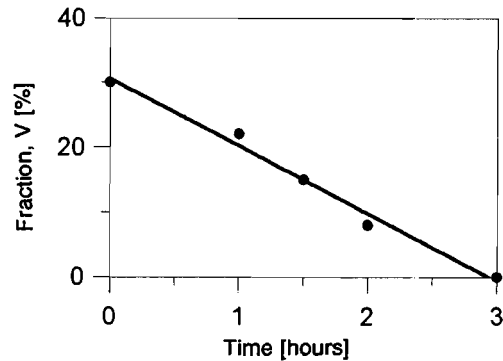


Fig.3. Amount of plates of the AlZn78 alloy against the ageing time at 533K.

The influence of ageing time at 533 K on the form of phases was shown in Fig.3. 100% of the irregular and globular types was observed after 3 hours of ageing, which was stated in the quantitative image analysis examinations.

Concluding, the optimum conditions of the heat treatment leading to obtaining structure characteristic for the superplastic deformation of Al78wt%Zn alloy are cooling of the alloy in the solid solution state without dendritic segregation at rate of about 2000 K/s and subsequent ageing at 533 K for 3 hours. The explanation of the advantageous influence of cooling rate on drop of the ratio of plate to globular fractions could be found in the diminishing amount of the nuclei of the monotectoidal transformation, occurring at high cooling rates as well as its degeneration on account of heterogeneous nucleation of the phases. The influence of the prolonged ageing time and high temperature of ageing on the growth of globular forms of grains resulted in the refinement of the plates and dislocation sets under thermal stresses as well as coagulation of this phase.

### Mechanical properties investigations

The mechanical investigations after heat treatment described above (tension and compression tests) and shown in Fig. 4 were carried out on the AlZn78 alloy deformed at rates  $v_1 = 1 \times 10^{-3} \text{ s}^{-1}$  and  $v_2 = 5 \times 10^{-3} \text{ s}^{-1}$  at temperatures from 293 to 573K. These investigations allowed to determine the range of deformation rates and temperature of superplastic deformation. The deformation temperatures, at which the lowest values of flow stress were obtained, slightly differed for the tension and compression tests. In the compression test the lowest flow stress was obtained at 503K (for the both deformation rates) but in the tension test the lowest value of flow stress was found to be between 523 to 573K. Obviously, the values of flow stress were smaller for the lower deformation rate. At temperatures below the lowest flow stress, the stress value increased very sharply but for the higher deformation temperatures the flow stress increase only slightly.

As for the compression test, the lowest stress amounted to 0.314 kp/mm<sup>2</sup> at the lower deformation rate at 503K and to 0.535 kp/mm<sup>2</sup> for the higher rate at the same temperature. For the lower deformation temperatures the values of the flow stress increased sharply and at 373K reached 2.3 and 4.5 kp/mm<sup>2</sup> for the lower and higher deformation rates, respectively. At room temperature they were 9.0 kp/mm<sup>2</sup> and 11.28 kp/mm<sup>2</sup>.

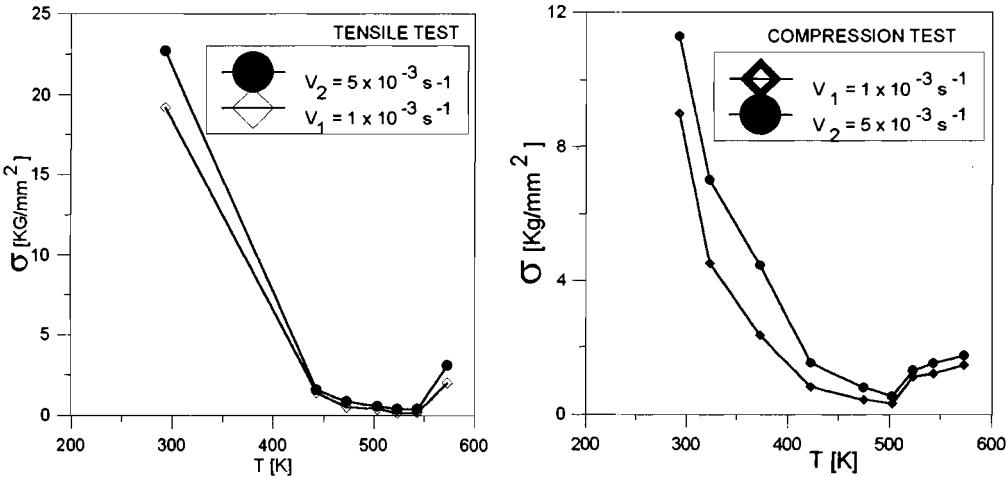


Fig.4. The dependence of flow stress on deformation temperature in tension test (left) and in compression test (right) of the AlZn78 alloy after heat treatment.

For the higher deformation temperatures, which were found to be optimum, the flow stress increased slightly and at 573K reached 1.45 kp/mm<sup>2</sup> and 1.74 kp/mm<sup>2</sup> for  $v_1$  and  $v_2$ , respectively. For the tension test the lowest stress was 0.16 kp/mm<sup>2</sup> and 0.38 kp/mm<sup>2</sup> for the lower and higher deformation rates respectively and, in temperature region from 523 to 543K the values were almost the same. For the lower deformation temperatures the flow stresses increased significantly. At higher temperatures, the flow stress also increased. It may be caused by the change of deformation mechanism i.e. a decrease of grain boundary sliding and mass transport and activation of other mechanisms like crystallographic slip and recrystallisation, respectively. It is important, that for the both tests the temperatures of the lowest flow stress differ by about 20 to 40 degrees. The reason of this phenomenon is not well understood, but it can be connected with a friction in the compression test increasing with the degree of deformation and grain boundary sliding conditions.

The tension test was also carried out on the AlZn76Cu2 and AlZn78Mg0.02 alloys (after the defined heat treatment) at the same strain rate as in the binary alloy (Fig. 5). The optimum conditions for the superplastic deformation i.e. the lowest value of the flow stress, were obtained at temperature range 523-543 K. The alloy with Mg addition reached a slightly smaller flow stress values than the alloy with copper. The lower superplastic elongation in the case of the alloy with Mg addition is most probably caused by a small magnesium containing precipitates at the grain boundaries affecting grain boundary sliding, while copper is distributed between aluminium and zinc solid solutions. The highest values of strain were obtained at lower temperatures than these at which the smallest flow stress was obtained in the binary alloy. The alloy with Cu addition revealed the highest strain (800%) at 503 K while the alloy with Mg addition reached the max. strain slightly above 400% at 523 K (Fig. 5.)

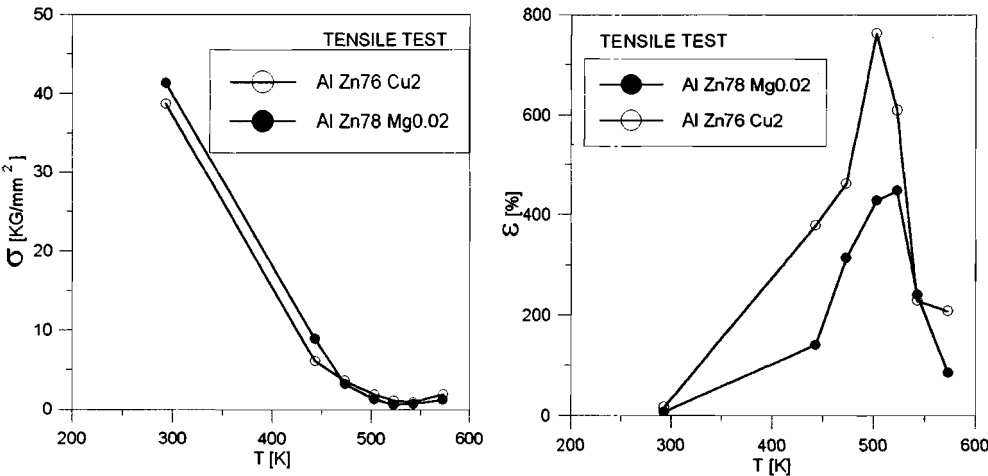


Fig. 5. The dependence of flow stress ( left) and max. strain (right) on deformation temperature in tension test of the AlZn76Cu2 and AlZn78Mg0.02 alloys after heat treatment.

### TEM investigations

Fig. 6 shows a transmission electron micrograph taken from as quenched AlZn78 alloy. One can see two regions of discontinuously formed  $\alpha$  and  $\beta$  particles; the latter visible in the dark contrast, fine lamellar of average thickness of 30 nm and globular (of average size 300 - 500 nm). Diffraction pattern (Fig. 6b) shows fairly uniform rings from  $\alpha$  and  $\beta$  phases what indicates that no strong texture exists in the initial stage. Fig. 7 shows a transmission electron micrograph taken after 48 hours of ageing at 533K. A significant growth of both phases up to the size of about 1  $\mu$ m is observed, combined with dissolution of the fine lamellae.

The alloy with 1.5wt% of copper addition has a similar structure after quenching to that presented in Fig.6. However, more elongated grains of larger diameter ( about 2  $\mu\text{m}$ ) exist after the ageing treatment (Fig.8). No additional precipitates due to the presence of copper can be seen. The microanalysis of both phases composition shows that aluminium rich  $\alpha$  phase contains 84wt % of Al, 15.7 wt% Zn and 0.3 wt % Cu, while the  $\beta$  phase 95 wt% Zn, 2.7 wt% Al and 2.3 wt% Cu. Most of copper is dissolved in the zinc rich phase and it is the zinc rich  $\beta$ -phase that is responsible for strengthening effect observed in the tensile test.

The structure of the AlZn78 alloy after superplastic deformation (Fig.9) shows that a globular size of grains is preserved, only some growth is observed. A low density of dislocations in both grains at various contrast conditions indicates that there is only a small activation of glide mechanism during the investigated superplastic deformation.

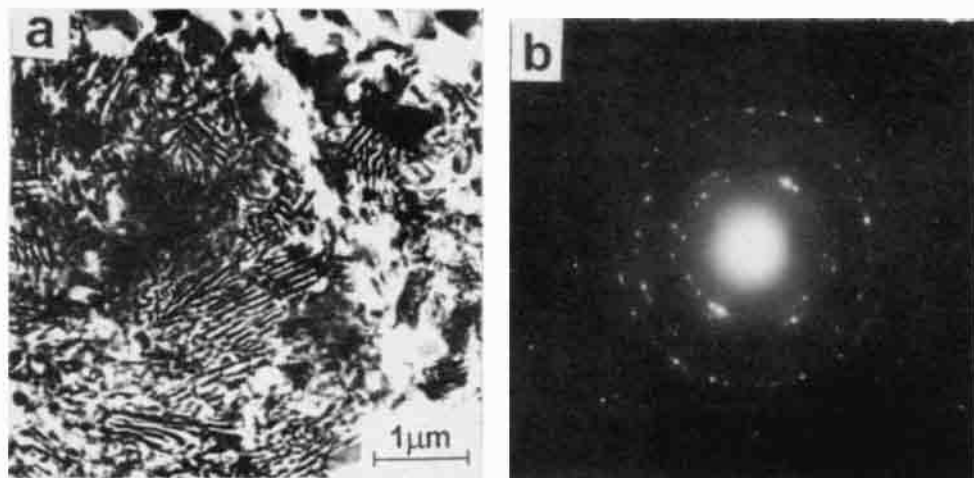


Fig.6 Alloy AlZn78 quenched from 643K to room temperature water. (a) Transmission electron micrograph, (b) Corresponding Selected Area Diffraction Pattern (SADP).

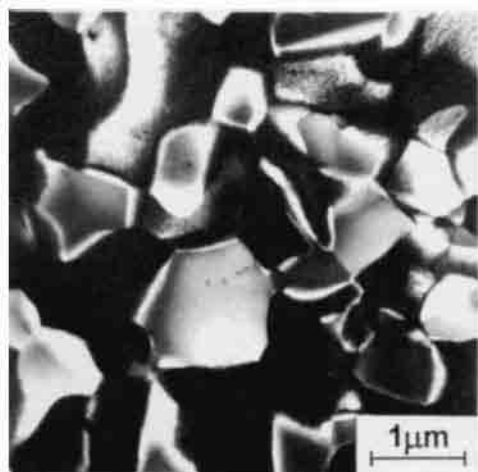


Fig.7 TEM micrograph taken of alloy AlZn78 quenched from 643K then aged for 48 hours at 533 K

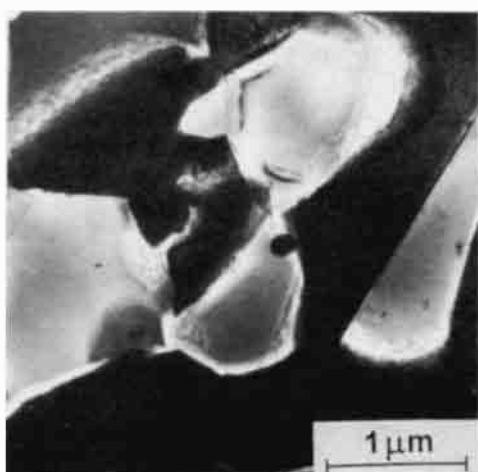


Fig.8 TEM micrograph of AlZn76.5 Cu1.5 alloy aged at 533 K for 48 hours.

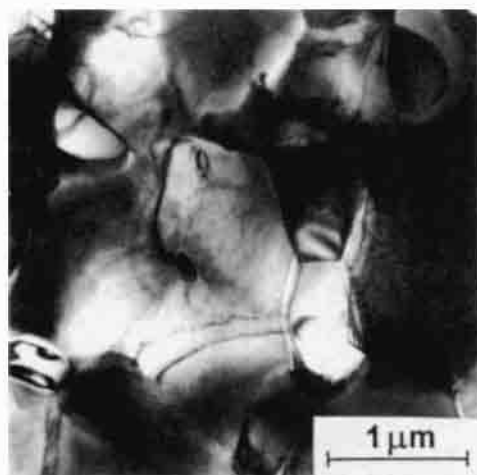


Fig. 9. TEM micrograph of alloy AlZn78 aged 48 hours at 533 K, then superplastically deformed at 533 K up to 200% of strain

### Texture investigation

Texture investigations were carried out on AlZn78 samples deformed by compression up to 50% at temperatures 293, 323, 423, 473, 503 and 543K and on a sample in the initial state. The basis for the texture investigations were the orientation distribution functions (ODF) which were calculated from pole figures in the space of Euler angles ( $j_1$ ,  $F$ ,  $j_2$ ). From the calculated ODFs it follows that the textures of both phases can be described in general by the fibre components with symmetry axis parallel to the compression axis<sup>22</sup>. A broad smoothed  $\langle 110 \rangle$  fibre as a dominating component and the  $\langle 100 \rangle$  fibre as a minor component occur in the Al phase. Three fibres in the direction  $\langle \bar{1}00 \rangle$ ,  $\langle 011 \rangle$  and  $\langle 01\bar{1} \rangle$  in the Zn phase are observed. The axes of all the fibres are lying in the plane  $j_2=0$  and that is the plane where all ODFs are plotted. It is visible in Fig. 10 that (0001), (0111) and (0110) fibre components are the most pronounced in the texture of the Zn phase in the initial state. After deformation at temperatures 293 and 423K the densities of the two strongest components i.e. (0001) and (0111) disappear, and at 473K the texture is totally smoothed, reaching the state of the lowest values (only traces of the (1211) fibre occur). Deformation at higher temperatures 503 and 543K leads to a strong increase of the ODF values for all three fibres, particularly for the (0001) one. The orientation distribution of the Al phase (Fig. 10) is nearly random in the initial state. The (110) and (001) fibre components become revealed after compression at increasing deformation temperature 293, 423 and 473K. The strong smoothing of components characteristic for superplastic deformation is observed in the Al phase at 503 K, which is higher than that at which the texture scattering phenomenon takes place in the Zn phase. After deformation at the higher temperature (543K) a relatively high concentration of orientation around the (110) fibre is visible. Besides the global changes in the texture described by the fibre components, definite regularities in the density distribution are observed also along the most pronounced (110) fibre in the Al phase. The profiles of distribution densities along the (110) fibre are shown in Fig. 11. The stable maxima at positions (011)[ $\bar{5}22$ ] ( $j_1=30^\circ$ ) and at (011)[ $\bar{0}11$ ] ( $j_1=90^\circ$ ), the heights of which rise with increasing compression temperature up to 473K are worth to be noted. These maxima change into a local minimum at 503K at which the deformation reveals superplastic properties. It is also notable that the density maximum in the neighbourhood of the extremum at (011)[ $\bar{5}22$ ] ( $j_1=30^\circ$ ) systematically shifts toward the (011)[ $\bar{0}11$ ]. Such a kind of tendency is not observed along the fibres in the Zn phase. Generally, only global changes, manifested by the occurrence of fibres and their disappearance when passing through the superplastic state, are visible in the texture of the Zn phase.

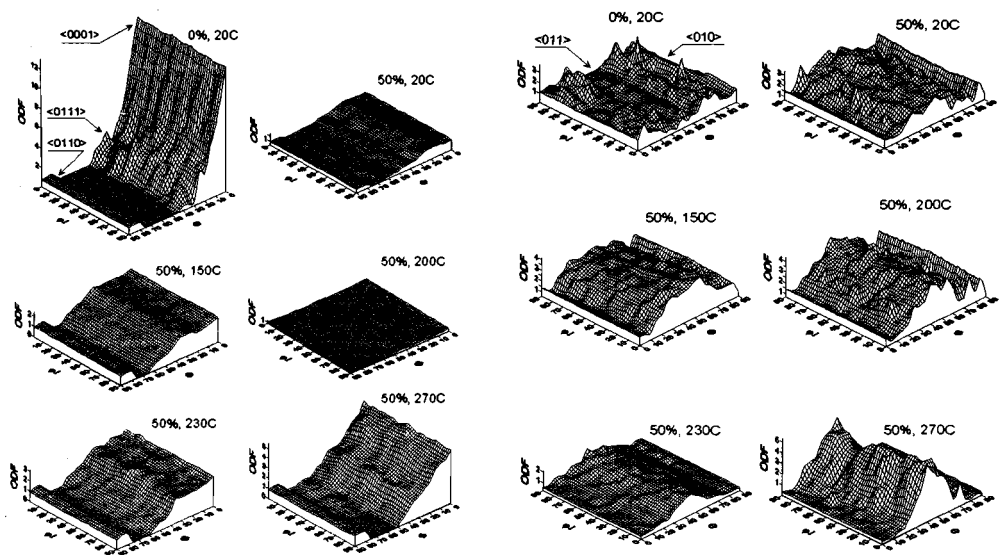


Fig.10. Distribution of orientation densities (ODF) for Zn phase (left) and for Al phase (right) of AlZn78 alloy

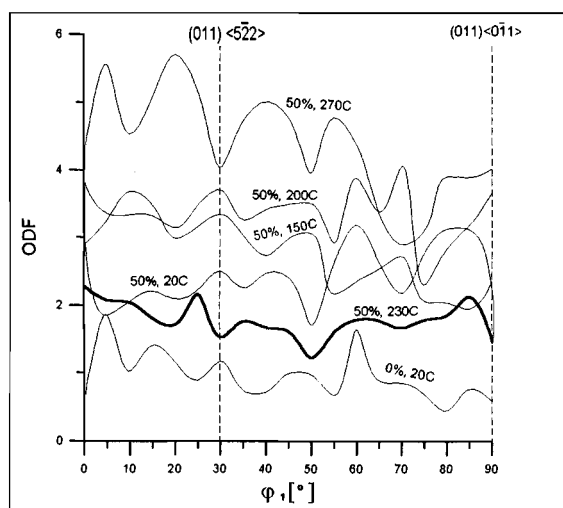


Fig.11. Profiles of orientation density along the most pronounced  $\langle 110 \rangle$  fibre of the AlZn78 alloy samples deformed at different temperatures.

More distinct regularities observed in the Al-phase allow us to distinguish dislocation slips expressed by the movement of orientation peaks along the fibres from the grain boundary sliding responsible for the smoothing effects and thus for the superplasticity of the alloy

## Industrial application

The backward press forming method was applied to produce the cups from the investigated alloys at temperature 523 K at a small deformation rate. The velocity of the displacement of the stamp was in the range of 1-10 mm/min.

A die stamping was produced in just one action. Stock (2) was fed into die (1) and the deformation to obtain a cup was performed by a stamp (3) which moved in a sleeve (4) driven by a piston of a hydraulic cylinder. The strain obtained was measured with strain gauge (5). The temperature of the deformed alloy was maintained by heating device (7) and controlled with sensor (8). After the deformation was completed shedder (9) driven by a piston (10) of hydraulic cylinder (11) ejected the cup. The whole press ram rested upon base (12).

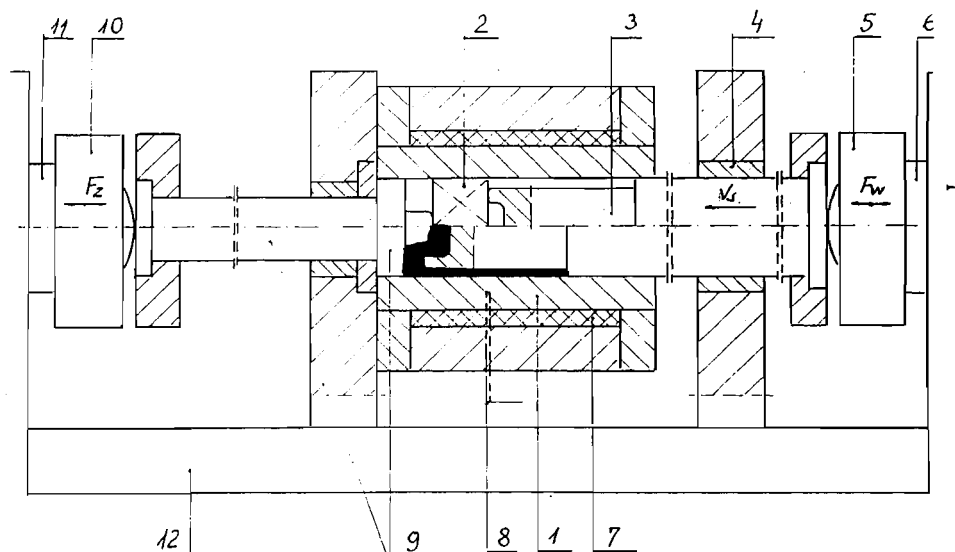


Fig.12. The scheme of the press for backward forming of cups in one action by means of the superplastic deformation mechanism. The deformation was done at temperature  $T = 523 \text{ K}$  and at stamp velocity of about  $1 \text{ mm/min}$ .

The average deformation and deformation rate in the wall of a moulded piece in the backward press forming are:

$$\varphi_b = \ln \frac{d_0 d_s}{d_0^2 - d_s^2} + \frac{d_0^2}{d_0^2 + d_s^2} \ln \frac{d_0}{d_s} \quad \varphi_b = \frac{3}{d_s} \varphi V_s [\text{s}^{-1}]$$

where:  $d_0$  - is the diameter of the die  
 $d_s$  - is the diameter of the stamp  
 $V_s$  - is the velocity of the stamp

The average deformation and deformation rate in the wall of a moulded piece in the synchronous press forming are:

$$\varphi_s = 2 \ln \frac{d_0}{d_m} \quad \varphi_s = \frac{6\varphi}{d_0} [\text{s}^{-1}]$$

where:  $d_m$  - is the diameter of the die stamping

The deformation rate in the synchronous press forming is much greater than in the backward press forming

$$\varphi_b \gg \varphi_s$$

In the press forming of cups from the investigated alloys the backward press forming method was applied.

## CONCLUSIONS

1. The globular shape of  $\alpha$  and  $\beta$  grains of size 1 - 2  $\mu\text{m}$  (allowing the best superplastic deformation conditions) was obtained at a highest cooling rate applied and aging temperature close to the eutectoid temperature.
2. The introduction of copper and magnesium improves mechanical properties at room temperature, although during the superplastic deformation the flow stress is only slightly higher than in the binary eutectoidal alloy.
3. Addition of copper and magnesium increases a tendency to form plates, but in the applied amount (1.5 wt% Cu and 0.02 wt% Mg) a close to globular structure can be obtained. Majority of copper enters the zinc solid solution (2.3 wt%), while only 0.3 wt% dissolves in aluminium.
4. The quantitative texture investigations (based on the orientation distribution function) allow to:
  - distinguish the crystallographic slips from the accompanying grain boundary sliding, which is responsible for superplastic deformation.
  - estimate the contribution of superplastic deformation in the total deformation process.

## ACKNOWLEDGEMENT

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## **EFFECT OF LIQUID PHASE ON SUPERPLASTICITY AT HIGH STRAIN RATES IN METALS AND THEIR COMPOSITES**

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### **ABSTRACT**

Superplasticity has been observed in many fine-grained metal-matrix composites, mechanically alloyed materials, and modified conventional alloys at extremely high strain rates ( $> 0.1 \text{ s}^{-1}$ ). These materials generally exhibited a strain rate sensitivity value of about 0.3 and a maximum elongation of over 300%. The origin of the observed phenomenon of superplasticity at very high rates was, in part, associated with fine grain sizes in these materials. However, a fine grain size was found to be a necessary but insufficient condition. The occurrence of the phenomenon appears to be also caused by the presence of a liquid phase, or in some cases a low melting point region, at the reinforcement-matrix interfaces or grain boundaries. In the present paper, experimental evidence will be given to show that marked changes in superplastic properties are closely related to incipient melting points in a range of materials. This suggests that the presence of a small amount of liquid phase at interfaces or grain boundaries not only enhances the strain rate for superplasticity, but also has a strong influence on the deformation mechanisms.

### **BACKGROUND**

Superplasticity, the ability of certain materials to undergo very large tensile strains, was first described in 1912 [1]. It became the subject of intense research in the early 1960s following the illustration of the potential commercial applications of superplasticity [2]. There have been enormous advances in the field of superplasticity since that time. The field has clear commercial applications, but also retains fascinating scientific challenges in understanding the underpinning physical mechanisms. Two of the most recent breakthroughs include the development of superplasticity in polycrystalline ceramics and the observation of superplasticity in metallic materials at high strain rates (also known as "HSRS"). Especially, the latter development is expected to have a great technological impact on the commercial applications of superplastic materials, since an increase in forming rate results in a reduction of forming time. In the following section we focus our attention on the physical origins of the HSRS phenomenon.

# DISCUSSION

## 1. Grain size effect

Grain size is obviously an important microstructural parameter contributing to HSRS. This is because grain-boundary sliding is the dominant high-temperature deformation mode in fine-grained, superplastic alloys. The constitutive or phenomenological equations for superplastic flow are generally expressed as [3],

$$\dot{\epsilon} = Ad^{-p}D\left(\frac{\sigma}{E}\right)^n, \tag{1}$$

where  $\dot{\epsilon}$  is the strain rate,  $A$  is a material constant,  $d$  is the grain size,  $p$  is the grain size dependence (which is typically 2 to 3),  $D$  is the diffusivity,  $\sigma$  is the stress,  $E$  is the modulus, and  $n$  is the stress exponent. According to Equation (1), refinement of the grain size by a factor of 2 would be expected to increase the optimum strain rate for superplastic flow by a factor of 4 to 8 depending on the precise grain-size relationship as described above.

An overview of the superplastic behavior of aluminum alloys to demonstrate the grain-size effect is depicted in Fig. 1, in which the quantitative relation between the logarithm of the optimum strain rate for superplastic flow and the grain size (plotted as the logarithm of reciprocal grain size) is clearly shown [4]. The slope of the curve in Fig. 1 is noted to be about 3.

It was pointed out by Nieh and Wadsworth [5] that fine grain size is a necessary but insufficient condition for HSRS. This conclusion resulted from the observation that many fine-grained composites are not superplastic at high strain rates. Evidently, in addition to grain size, microstructural factors, such as detailed structure and chemical composition at the reinforcement–matrix interfaces and grain boundaries, may play important roles.

## 2. Interfacial segregation effect

One of the microstructural factors is proposed to be solute segregation at grain boundaries in an alloy, or at reinforcement-matrix interfaces in a composite. Both grain boundaries and interfaces are preferential microstructural sites for solute segregation. In fact, numerous reports have shown that the presence of ceramic reinforcements can influence solute distributions in an alloy [6]. For example, a special FEM/STEM (field emission microscopy/scanning transmission electron microscopy) technique has been used to study solute segregation to SiC/Al alloys interfaces [7] and showed that the Mg and Cu concentrations at the SiC/matrix interfaces in an underaged 15 vol % SiC<sub>p</sub>-series 2000 Al (1.45 at. % Cu, 1.67 at. % Mg, 0.12 at. % Zr, 0.1 at. % Mn) could reach approximately 4.5 and 9 at. %, respectively, as shown in Fig. 2. Both the Mg and Cu segregation are expected to reduce the local melting point of the Al matrix near the interface region. Also, solute segregation changes the interfacial/grain-boundary chemistry and, thus, is expected to change the sliding mobility.

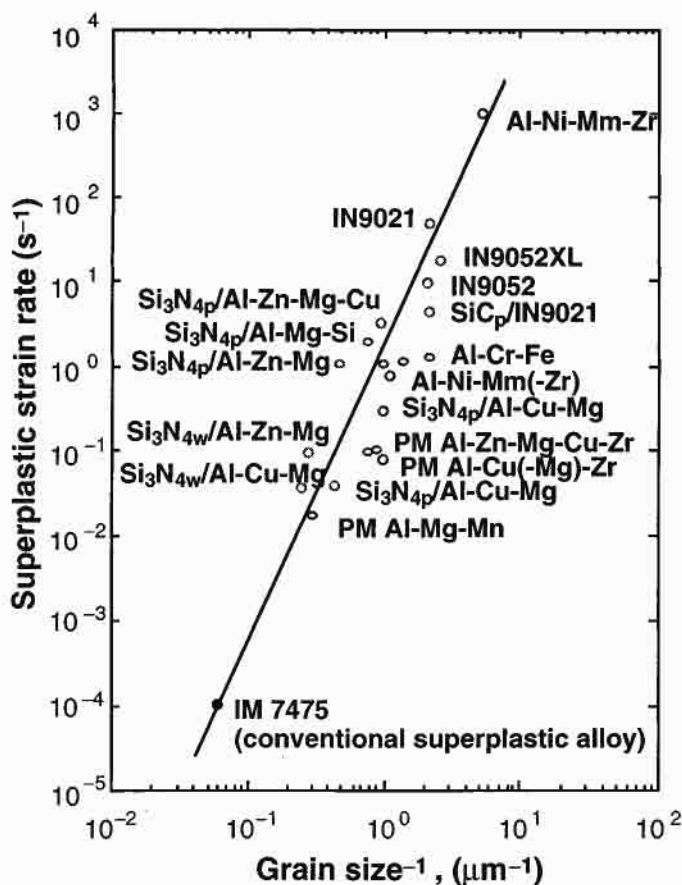


Fig. 1 The relationship between optimum superplastic strain rate and grain size for superplastic aluminum alloys (data from Ref. [4]). Subscripts "w" and "p" stand for whisker and particulate, respectively.

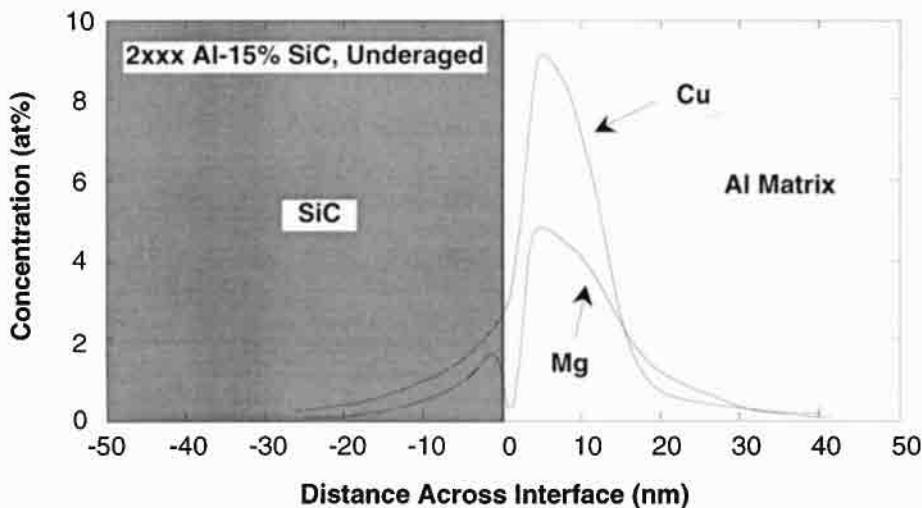


Fig. 2 Segregation of Cu and Mg at the SiC-series 2000 Al interface. The melting point of the interfacial region is expected to be reduced as a result of such segregation (data from Ref. [7]).

Therefore, although the test temperature for a 2124 Al composite may appear to be within the solid range of 2124 Al, because of the Mg segregation it may nonetheless be sufficiently high to result in local melting at the reinforcement-matrix interface. For example, a Mg concentration of over 6.5 at. % at the interface can by itself result in localized melting at as low as 465 °C! (According to binary phase diagrams, the effects of Mg and Cu on the melting point of Al are estimated to be approximately  $-6\text{ }^{\circ}\text{C/at. \% Mg}$  and  $-6.5\text{ }^{\circ}\text{C/at. \% Cu}$ ).

Solute segregation and local melting phenomena in several  $\text{Si}_3\text{N}_4/\text{Al}$  alloy composites have now been observed. For example, in addition to using differential scanning calorimetry (DSC) to characterize the incipient melting point, Koike *et al* [8, 9] employed an *in situ* TEM technique to examine the microstructure (Fig. 3) and chemical composition (Table 1) of both  $\text{Si}_3\text{N}_4/\text{Al-Mg}$  (5052 Al) interface and Al alloy matrix grain boundaries at the optimum temperature for superplasticity. Local melting, as a result of solute segregation, was specifically observed. As shown in Table 1, solute distribution at interface boundaries was apparently different than that at grain boundaries.

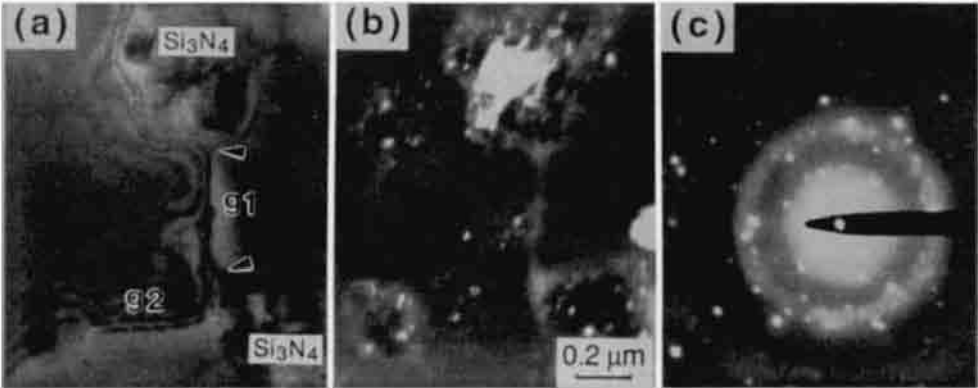


Fig. 3 (left) TEM bright-field and (middle) dark-field images, and (right) selected area diffraction pattern from a 20 vol%  $\text{Si}_3\text{N}_4/5052\text{ Al}$  composite at 548 °C. (from Ref. [8, 9])

Table 1 Concentration of major solute elements at grain boundary, interface, and matrix in the  $\text{Si}_3\text{N}_4/5052\text{ Al}$  composite

|                | Mg             | Si             | Cr   | O              | N              |
|----------------|----------------|----------------|------|----------------|----------------|
| Grain boundary | — <sup>a</sup> | 2.5            | 0.13 | 1.0            | 3.9            |
| Interface      | 9.3            | — <sup>b</sup> | 0.10 | 3.2            | — <sup>b</sup> |
| Grain interior | — <sup>a</sup> | — <sup>a</sup> | 0.18 | — <sup>a</sup> | — <sup>a</sup> |

<sup>a</sup> Too low.      <sup>b</sup> Strong peak.

## 2. Liquid phase effect

For the purpose of discussion, Table 2 summarizes HSRS data obtained from a number of Al alloys and composites. It was first noted by Nieh *et al* [5] that the optimum temperature for high strain rate superplasticity in an alloy is either above or close to the solidus temperature. This led them to suggest that the presence of a liquid phase might have contributed to the observed HSRS.

Table 2 HSRS aluminum alloys and composites [10]

|                                                                                                   | Test Temp., °C | Solidus, °C |
|---------------------------------------------------------------------------------------------------|----------------|-------------|
| Composites<br>( $\dot{\epsilon}$ =0.2–0.5 s <sup>-1</sup> , $\epsilon$ = 250–450%)                |                |             |
| β SiC <sub>w</sub> /2124 Al                                                                       | 525            | 502         |
| β Si <sub>3</sub> N <sub>4(w)</sub> /2124 Al                                                      | 525            | 502         |
| α Si <sub>3</sub> N <sub>4(w)</sub> /7064 Al                                                      | 525            | ~ 525       |
| β Si <sub>3</sub> N <sub>4(w)</sub> /6061 Al                                                      | 545            | 582         |
| 27 wt% β SiC <sub>w</sub> /7075 Al                                                                | ~500           | < 538       |
| Mechanically-alloyed Alloys<br>( $\dot{\epsilon}$ =1-50 s <sup>-1</sup> , $\epsilon$ = 300–1250%) |                |             |
| IN 9021                                                                                           | 450            | 495         |
| IN 9021                                                                                           | 550            | 495         |
| IN 90211                                                                                          | 475            | 495         |
| MA SiC <sub>(p)</sub> /IN9021                                                                     | 550            | 495         |
| IN9052                                                                                            | 590            | 593         |
| Alloys ( $\dot{\epsilon}$ =0.05–0.3 s <sup>-1</sup> , $\epsilon$ = 500–900%)                      |                |             |
| 7475 Al–0.9 wt% Zr                                                                                | 520            | < 538       |
| 7475 Al–0.7 wt% Zr                                                                                | 520            | < 538       |
| 2124 Al–0.6 wt% Zr                                                                                | 475            | 502         |

\*w = whisker; p = particulate.

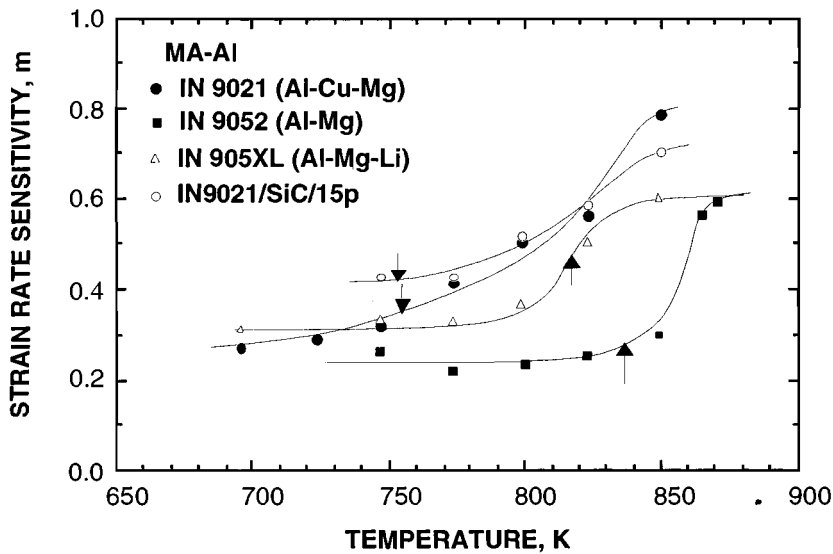


Fig. 4 Stress–strain rate behavior of several mechanically alloyed materials, showing the increase of  $m$  values at temperatures corresponding to the incipient melting point for each alloys (data from Ref. [11]).

To illustrate the liquid effect, Higashi *et al.* [11] recently performed experiments with several MA materials, including IN9021, IN9052, and IN905XL. The results, shown in Fig.

4, clearly indicate that the  $m$  values for these alloys are dependent upon the testing temperature. It is readily observed in the figure that all of the  $m$ - $T$  curves exhibit a sigmoidal shape. In the low-temperature region the  $m$  value is generally a constant and is relatively low (0.25–0.33; i.e.  $3 < n < 4$ ). The  $m$  value increases rapidly in the intermediate temperature range and reaches another plateau at high temperatures. In this high-temperature region the  $m$  value is normally over 0.5 ( $n < 2$ ), a typical value for a highly superplastic material. For example, the  $m$  value for IN9052 is a constant and is less than 0.3 at temperatures below 500 °C. It increases quickly above 540 °C, however, and approaches another constant value of about 0.6 at  $T > 600$  °C. In the case of IN9021,  $m$  even reaches a value of as high as 0.8 in the high-temperature region. For the purpose of illustration, all curves in Fig. 4 are marked by an arrow indicating the incipient melting points,  $T_i$ , for the material. It is evident that values of  $m$  increase drastically at  $T > T_i$ . A change in  $m$  from low- to high-temperature regions indicates a corresponding change in deformation mechanisms.

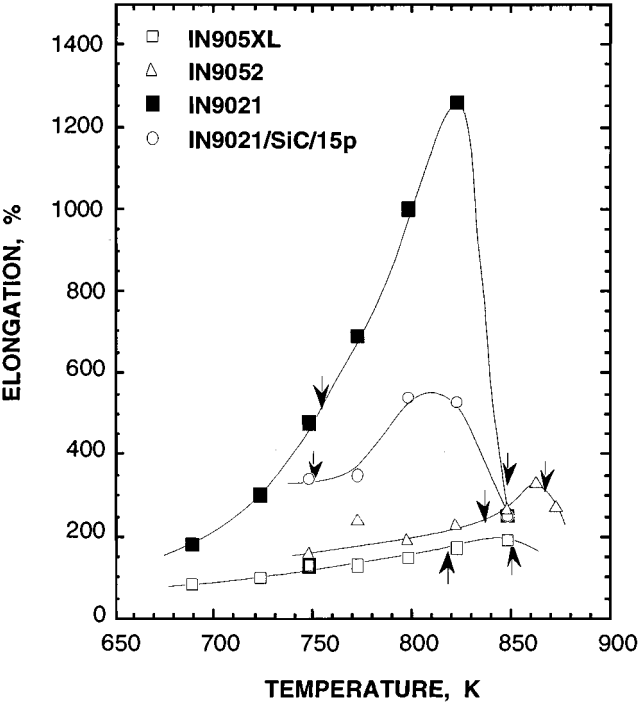


Fig. 5 Elongation-to-failure as a function of testing temperature for MA materials. /The left and right arrows on each curve indicate the incipient melting point and solidus temperature, respectively.

Higashi *et al.* [12] further demonstrated that testing temperature also strongly influences tensile elongation. For example, the total elongations-to-failure as a function of deformation temperature for the above superplastic MA materials are plotted in Fig. 5. Although there are different maximum values of elongation-to-failure for the different materials, it is readily seen that for a given material there is a maximum value of elongation-to-failure and that this maximum occurs at a characteristic temperature. Again, for the purposes of illustration all curves in Fig. 5 are marked by two arrows. The left-hand-side arrow indicates  $T_i$ , and the right-hand-side arrow indicates the solidus temperature,  $T_s$ . Generally the elongation-to-failure values are noted to increase at temperatures greater than  $T_i$ . Once the elongation-to-failure value reaches a maximum, it

decreases very rapidly with further increase in temperature. The maximum value of elongation-to-failure is noted to occur always at a temperature that is between  $T_i$  and  $T_s$ . This general trend also prevails in several HSRS Al composites [12], as shown in Fig. 6. There is yet another dramatic illustration of the effect of testing temperature, and thus the presence of a liquid, on tensile ductility. Shown in Fig. 7 is the tensile elongation of 7475 Al as a function of testing temperatures, recently reported by Higashi [13]. Tensile elongation is noted to increase sharply when a small amount of liquid phase is present at grain triple points. It is worth noting that conventional superplastic 7475 Al with a grain size of 15  $\mu\text{m}$  exhibits a 1000% elongation at 777K and a strain rate of  $\sim 2 \times 10^{-4} \text{ s}^{-1}$ .

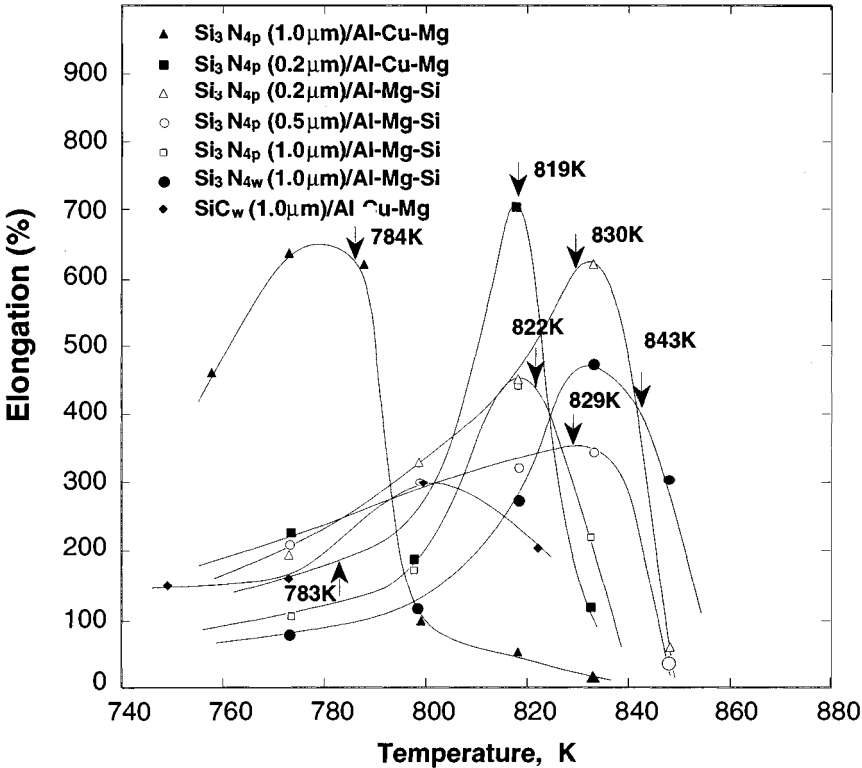


Fig. 6 Elongation to failure as a function of testing temperature for Al-matrix composites. Incipient melting points for each alloy are indicated by arrows.

At  $T \geq T_i$ , but at temperatures near  $T_i$ , only a small amount of liquid phase is present. The liquid phase would be expected to segregate to grain boundaries, and particularly at grain triple junctions. As shown in Fig. 8, when the liquid phase is very thin, atoms in the solid state across two adjacent grains can still experience a traction force,  $T_{gb}$ , from each other. In other words, the grain boundary can sustain an applied tensile force. Also, shear stresses can be transferred across the boundary. When  $T \gg T_i$ , and  $T$  is close to  $T_s$ , macroscopic melting begins to occur, the liquid phase is thick, and atoms across two neighboring grains can no longer experience traction from each other. In other words, the grain boundary can no longer support an applied tensile force and shear stresses cannot be transferred across the boundary. Also, grain-boundary cavitation becomes extensive. Ductility in this latter case is therefore limited.



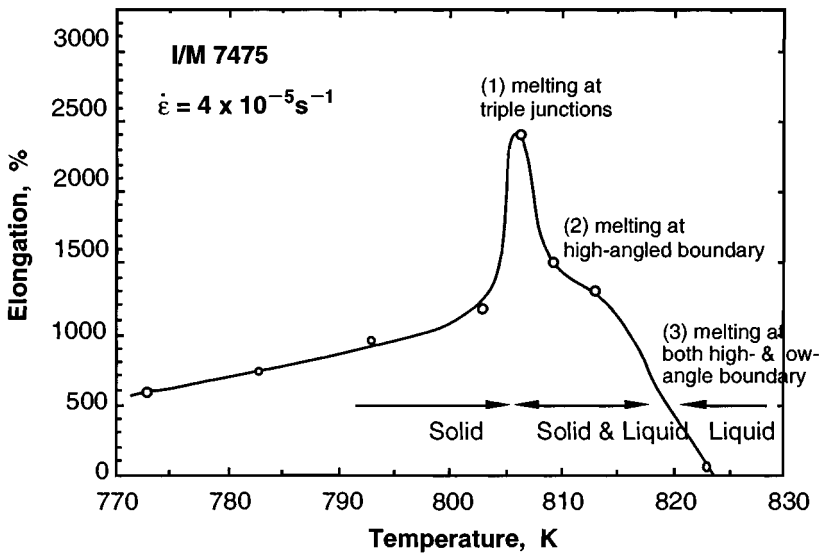


Fig. 7 Elongation of superplastic 7475 Al (grain size = 15  $\mu\text{m}$ ) as a function of testing temperature. (data from Ref. [13]).

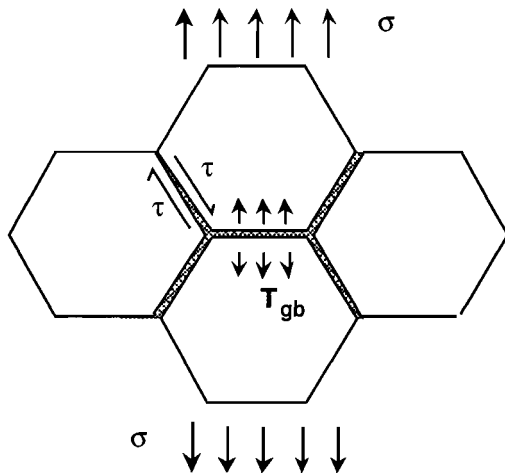


Fig. 8 Schematic representation of grain structure in the presence of grain-boundary liquid phases.

There apparently exists a critical amount of liquid phase for the optimization of grain/interface boundary sliding during superplastic deformation. The optimum amount of liquid phase may depend upon the precise material composition and the precise nature of a grain boundary or interface, such as local chemistry (which determines the chemical interactions between atoms in the liquid phase and atoms in its neighboring grains) and misorientation. The existence of an equilibrium thickness of intergranular liquid phase in ceramics has been discussed [14]. This area of detailed study in metal alloys has not been addressed.

A full mechanistic description of HSRS is still unavailable, despite some limited efforts [5, 15]. It is unclear whether a model based on conventional superplasticity modified by the presence of a liquid phase can describe the phenomenon or whether it is necessary to invoke a completely-new model.

## ACKNOWLEDGMENT

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# HYDROGEN AS A USEFUL ALLOYING ELEMENT IN TITANIUM ALLOYS

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## INTRODUCTION

For many years hydrogen was considered as a deleterious impurity which deteriorates mechanical properties of materials. This is clearly illustrated by hydrogen embrittlement of ferrous metals and alloys. The main effort of the research was aimed therefore at the study of hydrogen embrittlement and at the ways to avoid it<sup>1</sup>.

But numerous papers published during recent decades showed that hydrogen can be a very useful alloying element for production of new materials (such as hydrogen accumulators, neutron absorbers, *etc.*) or new technologies for alloy processing with improved treatment parameters as well as with the improved final properties of the alloys<sup>2</sup>.

There are several reasons which made hydrogen processing most applicable to titanium alloys:

1. Titanium alloys are widely applied in aviation, rocket engineering and ship building due to their high strength, corrosion resistance and the small specific weight.
2. Their deformation is normally performed at temperatures as high as 900–950°C or more due to their low ductility at moderate temperatures.
3. Titanium and most of its alloys readily absorb and evolve hydrogen due to high solubility and diffusion mobility of hydrogen at moderate temperatures.
4. Hydrogen effect on the mechanical properties results in markedly enhanced ductility and lowered flow stress of the alloys therefore they become workable at much lower temperatures.

This induced an increasing number of papers devoted to the study of the hydrogen effect on the mechanical properties of titanium alloys<sup>3–10</sup>. Some interesting effects of hydrogen in titanium and its alloys are discussed below on the basis of the experimental data obtained at ISSP RAS (the early experiments were carried out in co-operation with the Institute of Metal Physics UD RAS).

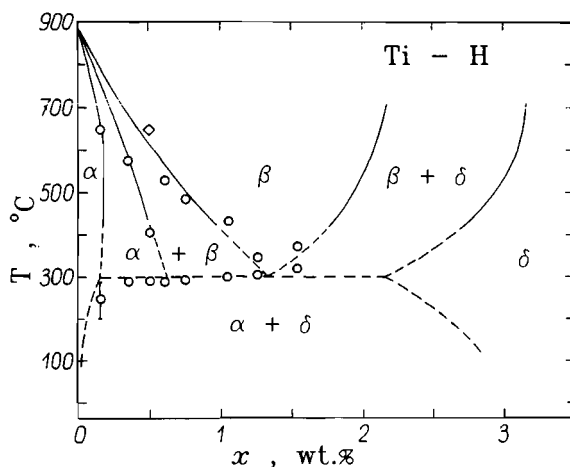


**Figure 1.** Phase diagram of the Ti - H system. Points are related to the anomalous ductility behavior.

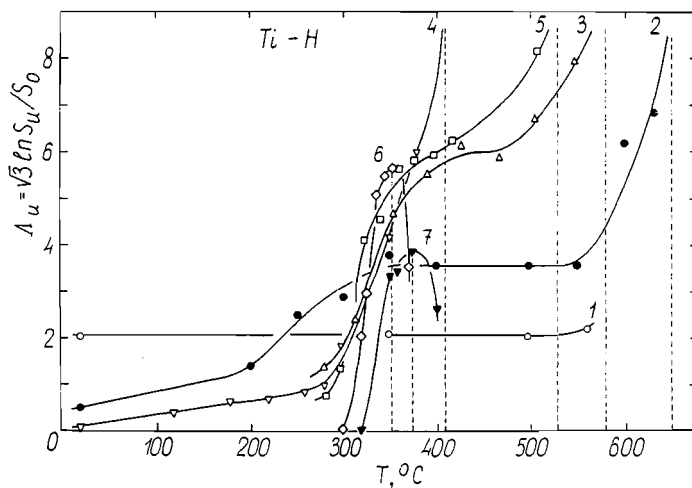


**Figure 2.** Ductility of Ti- $x$ H alloys in dependence on temperature. Here ductility is a logarithmic function of the area reduction in tensile tests. Hydrogen contents are 0 (curve 1), 0.16 (2), 0.35 (3), 0.50 (4), 0.61 (5), 1.25 (6) and 1.54 wt.%.

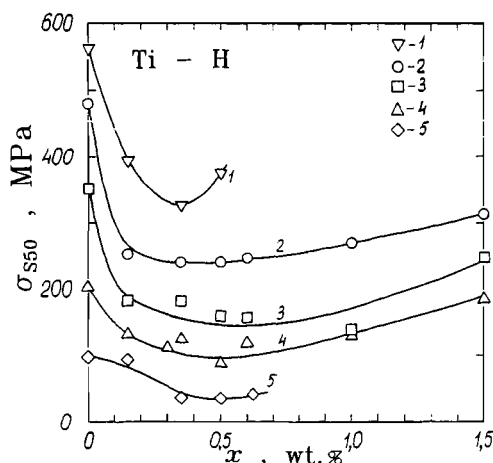


**Figure 3.** Flow stress of Ti- $x$ H alloys on compression at several temperatures and the accumulated strain  $\epsilon = 50\%$ . Temperature are 300 (curve 1), 400 (2), 500 (3), 600 (4) and 700°C (5).

## EXPERIMENTAL

Hydrogen effect on the mechanical properties discussed below was studied on several  $\alpha$  and  $\alpha + \beta$  alloys with the following nominal composition of metallic components (Russian trade marks given in parentheses): commercial titanium of nominal purity 99.3% (VT1-0), Ti-6Al-2Zr-1.5V-1Mo (VT20), Ti-6Al-4.5V (VT6), Ti-6Al-2.5Mo-2Cr (VT3-1), Ti-4Al-1.5Mn (OT4), Ti-6.5Al-4Mo-2Sn-0.6W-0.2Si (VT25u) and others. The main features of their stress-strain behavior due to hydrogenation were much similar, but some individuality was characteristic of each alloy.

The hydrogen treatment procedures, tensile, compression and torsion tests at fixed temperatures, transmission electron or optical microscopy at room temperature as well as X-ray diffraction measurements were detailed elsewhere<sup>11,12</sup>. All experiments were performed so as to compare properties of the same alloy, but modified using different treatment procedures.

The phase diagram and other properties were measured on metal Ti with the total impurity content less than 0.02%.

## STRESS-STRAIN BEHAVIOR OF HYDROGENATED ALLOYS

The hydrogen effect on ductility and the flow stress will be considered first on the example of non-alloyed titanium. The Ti - H phase diagram is given in Fig. 1, and Fig. 2 shows the temperature dependence of ductility of Ti- $x$ H alloys,  $\Lambda_u$ , for several  $x$  values. Tensile tests were run at a rate  $\dot{\epsilon} \approx 10^{-3} \text{ s}^{-1}$ . Ductility of the commercial

metal began appreciably growing over 550°C. Low  $\Lambda_u$  values were observed in the range  $T = 20$  to 250°C at  $x = 0.15$  to 1.0, but  $\Lambda_u$  sharply increased near 300°C. A plateau-like regions followed by the second rapid increase in  $\Lambda_u$  were characteristic of higher test temperatures. *E.g.*, ductility of the Ti-0.16H alloy which was brittle at room temperature exceeded that of the basic metal already at 250°C, remained constant in the range 300 to 600°C, and demonstrated further sharp increase over 600°C. The sharpest increase in ductility at 280 to 400°C had the Ti-0.5H alloy.

Other ductility behavior showed alloys with  $x = 1.25$  and 1.54 whose ductility  $\Lambda_u(T)$  jumped near 300°C, passed through a maximum at about 350°C, passed through a maximum at about 350°C, and again decreased at higher test temperatures. Points in Fig. 1 correspond to temperatures of anomalous  $\Lambda_u(T)$  behavior for appropriate hydrogen contents. A clear correlation is observed between the ductility anomalies and special lines in the phase diagram, i.e., all points fall at the boundaries of the two-phase regions or at the line equidistant from these boundaries.

The second interesting effect of hydrogen alloying concerned the changes in flow stress. Concentrational curves,  $\sigma(x)$ , in the range 300 to 750°C had a minimum which was more prominent for developed plastic flow (see Fig. 3). Strain hardening of hydrogen-alloyed titanium was less than that of the basic metal over 350–400°C therefore compressive strain of 10 to 20% resulted in lower values of  $\sigma$  for hydrogen-alloyed samples compared to hydrogen-free ones. *E.g.*, the  $\sigma_{50}$  values at  $\epsilon = 50\%$  for samples with  $x = 0.35$  to 0.60 were only 30 to 60% of that for basic metal (Fig. 3).

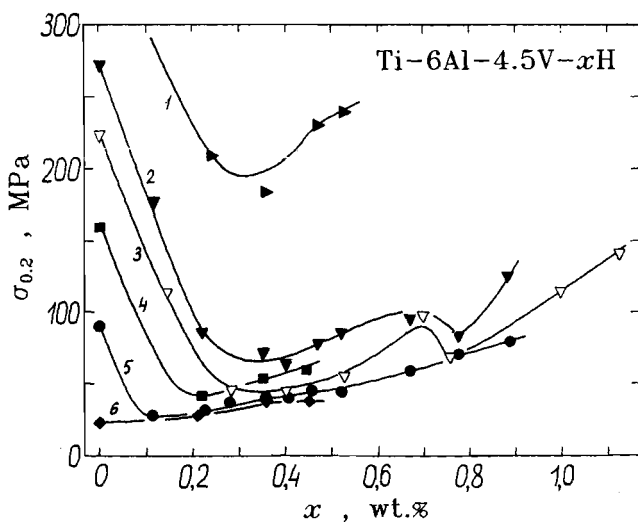


**Figure 4.** Yield stress of the Ti-6Al-4.5V alloy in dependence on hydrogen content at several temperatures. Temperature are 688 (curve 1), 745 (2), 735 (3), 806 (4), 867 (5) and 930°C (6).

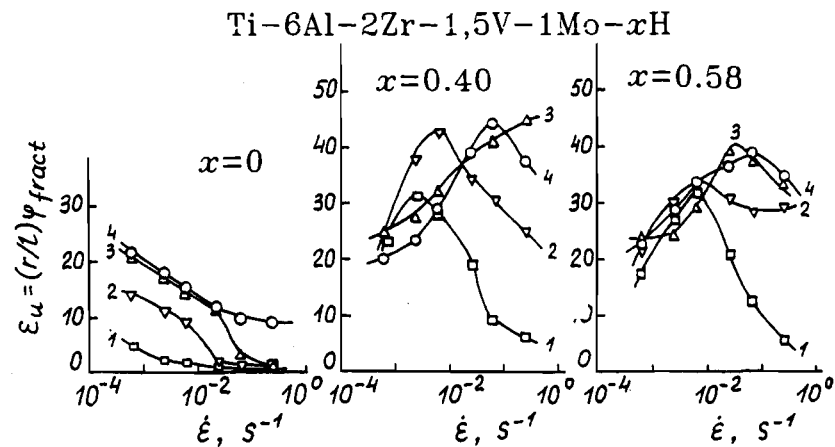


**Figure 5.** Ductility (ultimate angle strain) of the Ti-6Al-2Zr-1.5V-1Mo-xH alloys in dependence on the strain rate in torsion tests at 607° - 1, 660° - 2, 720° - 3 and 780°C - 4.

Similar phenomena were observed on the high-strength industrial titanium alloys, as illustrated for the Ti-6Al-4.5V alloy in Fig. 4.

The third effect concerns the strain-rate dependence of mechanical properties. A more detailed study was carried out on a standard commercial Ti-6Al-2Zr-1.5V-1Mo (wt.%) alloy. Figures 5 and 6 show typical ductility patterns for alloys with several hydrogen contents in dependence on temperature or torsional strain rate<sup>13</sup>. It is evident from Fig. 6 that ductility curves,  $\epsilon_u(\dot{\epsilon})$ , of the hydrogenated alloy have distinctly observed maxima while ductility of the basic alloy decreases throughout the strain-rate range studied,  $\dot{\epsilon} = 5 \cdot 10^{-4}$  to  $5 \cdot 10^{-1} \text{ s}^{-1}$ . The effect of hydrogen-enhanced ductility expressed as a ratio  $\alpha = \epsilon_u(x)/\epsilon_u(0)$  is represented in Fig. 7. Function  $\alpha(\dot{\epsilon})$  is a curve with a maximum and attains a value of about 27 at  $T = 607^\circ\text{C}$  and  $\dot{\epsilon} = 10^{-2} \text{ s}^{-1}$  and about 45 at  $T = 660^\circ\text{C}$  and  $\dot{\epsilon} = 10^{-1} \text{ s}^{-1}$  for  $x = 0.58$ , i.e., torsional ductility of the hydrogenated alloy at these conditions is 27 and 45 times that of the same alloy without hydrogen, respectively.

Certain peculiarity was characteristic of each alloy studied. For example, any hydrogen content embrittled the non-alloyed titanium at room temperature. Other behavior was observed on the Ti-6Al-4.5V alloy at room temperature and low strain rates. The ultimate compressive strain of this alloy without hydrogen was about 8.5% at  $\dot{\epsilon} = 10^{-3} \text{ s}^{-1}$  while hydrogen alloying to  $x = 0.27$  increased this value to about 20% and to 10 to 14% at other  $x$ .

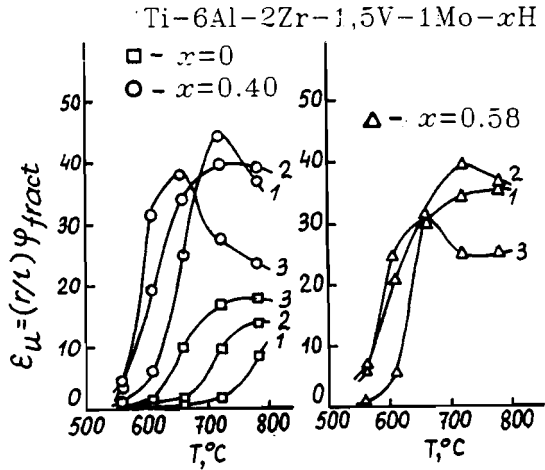


**Figure 6.** Ductility of the Ti-6Al-2Zr-1.5V-1Mo-xH alloys in dependence on temperature at fixed strain rates of torsion:  $\dot{\epsilon} = 0.25 \text{ s}^{-1} - 1$ ,  $\dot{\epsilon} = 0.025 \text{ s}^{-1} - 2$  and  $\dot{\epsilon} = 0.0025 \text{ s}^{-1} - 3$ .



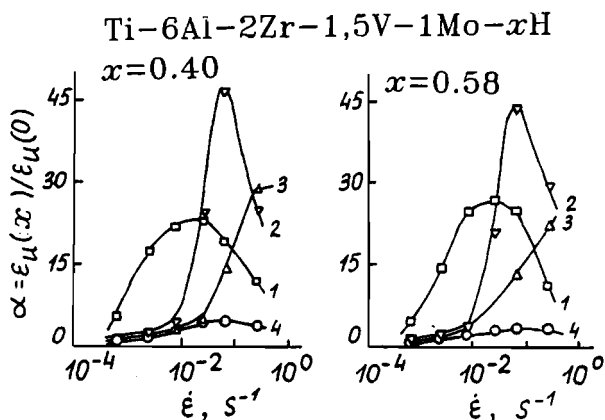


**Figure 7.** Hydrogen-induced ductility enhancement of the Ti-6Al-2Zr-1.5V-1Mo alloy in torsion tests at temperatures 607° - 1, 660° - 2, 720° - 3 and 780°C - 4.

## HYDROGEN/STRAIN EFFECT ON THE GRAIN STRUCTURE

Phase composition and grain structure of Ti-6Al-2Zr-1.5V-1Mo-0.35H alloy after heat treatment and after deformation were studied in comparison with the basic alloy. After hydrogenation and cooling to room temperature the structure of the specimens was  $\alpha'$ -martensite with 20-25% of the  $\beta$ -phase.

The hydrogenated alloy transformed to the single-phase state,  $\beta$ , on heating to 850°C. The single-phase structure retained after cooling the specimens down to 810°C (Fig. 8a). After cooling below 810°C, the  $\alpha$ -phase was observed inside the large  $\beta$ -grains as needle-shaped particles. The volume content of the  $\alpha$ -phase did not exceed 10% at 780°C (Fig. 8b). Samples cooled from 890 to 630°C and exposed at this temperature showed the highest degree of the  $\beta \rightarrow \alpha$  transformation (Fig. 8c).

Specimens strained above 810°C retained the single  $\beta$ -phase structure. The  $\beta$  grains became markedly less in size due to their fragmentation and dynamic recrystallization. The grain structure of the alloy strained at 780°C and cooled to room temperature consisted of dynamically recrystallized grains of the  $\beta$ -phase ( $\sim 12 \mu\text{m}$  in size) and of small equiaxial grains of the  $\alpha$ -phase ( $\lesssim 4 \mu\text{m}$  in size) uniformly distributed over the volume. The amount of the  $\alpha$ -phase was 16 vol.% at 780°C, but increased to  $\sim 50\%$  as the deformation temperature decreased to 730°C (Fig. 8d). So fine two-phase structure was formed at this test temperature due to two processes: due to fragmentation and spheroidation of the initial  $\alpha$ -phase needles and due to martensitic phase transformation in the supercooled  $\beta$ -phase. A similar grain structure was observed after deformation at 680°C, but for the smaller grain size and a larger amount of the  $\alpha$ -phase.

Thus, hydrogenation and straining of the alloy at 680-780°C followed by final outgassing results in a very fine grain structure which is favorable for the mechanical properties of the final product.

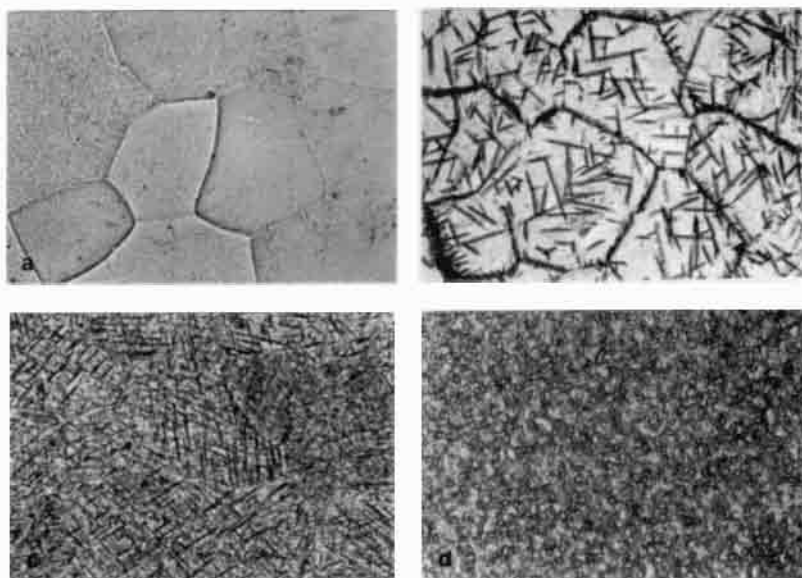


**Figure 8.** Grain structure of the Ti-6Al-2Zr-1.5V-1Mo-0.35H alloy after heating to 890°C followed by cooling to 810°C (the  $\beta$ -phase region) - a, to 730°C (the  $\alpha+\beta$  region) - b, to 630°C (the  $\alpha+\beta$  region) - c, and strained at 730°C - d.

The  $\alpha - \beta$  transformation has a large hysteresis in hydrogenated titanium alloys, and different thermal treatments change their phase content. Various degrees of metastability due to hysteresis are implicit for the alloys after different thermal treatments. Metastable phases undergo transformation to a more equilibrium state during deformation, which can effect the flow of the alloy. Below we consider the effect of the thermal pre-strain treatment on ductility on the strength of the Ti-6Al-2Zr-1.5V-1Mo- $x$ H alloys<sup>14</sup>.

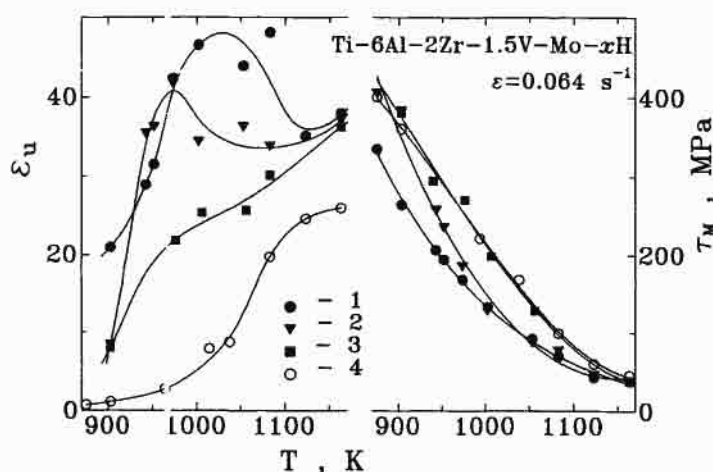


**Figure 9.** Thermal dependence of the strength and torsional ductility of Ti-6Al-2Zr-1.5V-1Mo- $x$ H alloys at  $\dot{\epsilon} = 0.064 \text{ s}^{-1}$ . Curves 1 and 2 are for non-equilibrium phase states, 3 is for the equilibrated state (all at  $x = 0.35$ ), and 4 is for  $x = 0$ .

This effect was estimated from the experimental comparison of the stress-strain properties in three sample series which were brought to different phase contents by means of heat treatment. All samples were hydrogen-alloyed to  $x = 0.35$  at  $T = 1053$  K, then furnace cooled. Before straining, samples of the first series were maintained at the test temperature for 0.5 h. Series 2 samples were heated to the  $\beta$ -phase,  $T = 1163$  K, for 15 min, then cooled to the test temperature and treated like series 1 samples. The phase content in the third series was equilibrated by heating to 1163 K and slow cooling to 903 K before the test temperature was fixed.

The effect of thermal pre-strain treatment on the torsional ductility of the alloys is shown in Figure 9. The curve numbers correspond to the sample series numbers. The basic alloy,  $x = 0$ , is represented for comparison as series 4. The series 1 samples had the highest ductility. That of the  $\beta$ -treated series 2 samples showed a similar thermal dependence below  $\sim 970$  K, but it was lower at 1000 to 1100 K. Ductility of the equilibrated series 3 samples did not show a maximum in its thermal dependence, but it exceeded ductility of the basic alloy.

These experiments illustrate an essential contribution to the plastic flow from phase transformations of metastable states.

## HYDROGEN EFFECT IN TITANIUM POWDER

In the previous Sections, bulk specimens were alloyed with hydrogen from the gas phase. It was interesting to see whether hydrogen affects the mechanical properties of titanium in a similar way if metal is in a powder state and hydrogen is introduced by mechanical mixing of the metal powder with titanium dihydride, or the interparticle boundaries are an insurmountable obstacle for hydrogen and eliminate the effects observed in bulk specimens.

To study this, mixtures were prepared from titanium and titanium dihydride powders sifted through a  $50\text{-}\mu\text{m}$  mesh sieve<sup>15</sup>. The basic materials were commercial titanium powder and  $\text{TiH}_2$  blended in a weight ratio of 8 : 1. The average hydrogen content was thus 0.5 wt.%. Specimens of the mixture were compacted at a hydrostatic pressure of 9 kbar and  $T = 250^\circ\text{C}$ , the treatment time being 5 min. The density of the compacted specimens was  $4.32 - 4.33\text{ g}\cdot\text{cm}^{-3}$ , which is more than 99.5% density of bulk titanium alloyed with 0.5wt.%H. The yield stress, the ultimate stress and the ultimate strain at  $20^\circ\text{C}$  were, respectively,  $\sigma_{0.2} = 736\text{ MPa}$ ,  $\sigma_u = 909\text{ MPa}$  and  $\epsilon_u = 4.2\%$ . The specimens were finally turned on a lathe to cylinders of 7 mm diameter and 12 mm height, then subjected to compression tests using an *Instron* machine at a strain rate of  $1\text{ mm}\cdot\text{min}^{-1}$  at fixed temperatures of 500, 600 and  $700 \pm 5^\circ\text{C}$ . For the sake of comparison, some specimens were outgassed by vacuum annealing at  $800^\circ\text{C}$  and tested under the same conditions.

Fig. 10 shows that the flow stress of the hydrogen-alloyed compacts is essentially less than that of the outgassed ones at all test temperatures. The flow stress relation between the hydrogen-alloyed and outgassed compacts depended on the strain. At equal strains at test temperatures, this ratio could achieve 2 or more. Thus, the effect of hydrogen on the properties of compacted powders is much similar to that observed on bulk titanium.

This stress-strain behavior is consistent with the optic metallographic data which evidenced partial redistribution of hydrogen over the powder particles when the compacting temperature was increased to  $400^\circ\text{C}$  and uniform hydrogen distribution on additional annealing or during plastic deformation at  $T \geq 500^\circ\text{C}$ .

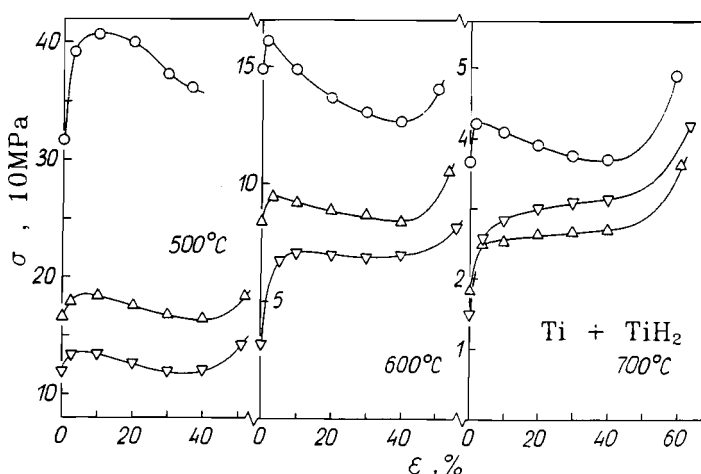


**Figure 10.** Hydrogen effect in compacted powder mixtures Ti + TiH<sub>2</sub> (8 : 1). Compacted at 9 kbar -  $\nabla$ , additionally annealed in vacuum at 735°C for 10 min -  $\Delta$ , outgassed -  $\bigcirc$ .

## PRESSURE-INDUCED DUCTILITY INCREASE IN Ti-H ALLOYS

Mechanical properties of hydrogenated titanium alloys are strongly dependent on the applied stress tensor, especially on its hydrostatic component. This was illustrated by the high-pressure tensile and extrusion tests on the Ti-6Al-2.5Mo-2Cr alloy and the same alloy hydrogenated to  $x = 0.15$  wt.%H. Tests were carried out using the apparatus at the Institute of Metal Physics UD RAS operating at hydrostatic pressures of machine oil to 15 kbar and temperatures to 250°C.

The basic alloy at atmospheric pressure and  $T = 20^\circ\text{C}$  demonstrated the per cent elongation  $\delta = 31\%$  and the per cent reduction  $\psi = 65\%$  while plastic properties of the hydrogenated alloy were close to zero. But an opposite relation was observed in tensile tests under a pressure of 6.5 kbar. The plastic properties of the hydrogenated alloy increased to  $\delta = 33\%$  and  $\psi = 83\%$  at  $P = 6.5$  kbar and  $T = 20^\circ\text{C}$  while those of the basic alloy changed only slightly (Fig. 11).

A corresponding pressure effect on the flow stress was observed on hydrostatic extrusion of conical specimens of the same alloy through a die of 5 mm dia at 220°C. The basic alloy was extruded at  $P = 12$  kbar up to the area ratio equal to 4.1 while the alloy hydrogenated to  $x = 0.20$  extruded to the area ratio of 7.6 even at a lower pressure,  $P = 11$  kbar<sup>9</sup>. Similar pressure/hydrogen effects on the flow stress were also observed on hydrostatic extrusion of ZrH<sub>x</sub>, VH<sub>x</sub> and Nb<sub>x</sub> alloys with  $x = 0$  and 0.1–0.2 wt.%.

## PHASE TRANSFORMATIONS IN Ti-H ALLOYS UNDER PRESSURE

The high-pressure study on the Ti-H alloys showed stress-strain properties are not the only ones which are affected by pressure, but phase equilibria are also strongly dependent on this parameter<sup>16</sup>. A new  $\zeta$ -phase and a corresponding single phase region in the isobaric  $T - C$  section of the  $T - P - C$  phase diagram appear in the

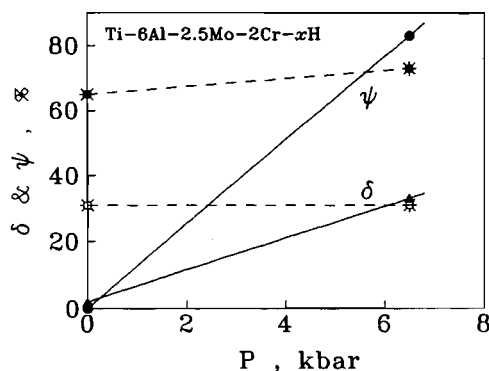


**Figure 11.** Effect of hydrostatic pressure on elongation  $\delta$  and area reduction  $\psi$  of the Ti-6Al-2.5Mo-2Cr- $x$ H alloys at room temperature tension,  $x = 0$  (dashed line) and 0.15 (solid line).

near-eutectoid alloys at  $P \geq 20$  kbar. The temperature range of this region is extended as pressure is increased. According to the *in situ* X-ray data, the  $\zeta$ -phase has a tetragonal structure whose lattice parameters relate as  $c/a = 0.89$ . After quenching from the  $\zeta$ -phase region under high-pressure and subsequent decompression to  $P = 1$  atm at 80 K, the TiH<sub>~0.75</sub> alloys were single-phase. The quenched metastable  $\chi$ -phase also has a tetragonal structure, but  $c/a = 0.95$ . Contrary to the stable phases, hydrogen occupied the octahedral interstitial sites, and the superconducting temperature increased to 4.3 K. Numerous phase transformations were observed on heating the  $\chi$ -phase until its return to the equilibrium state<sup>17</sup>. There were found serious arguments for thermodynamic stability of the ordered  $\gamma$ -phase at normal conditions<sup>16</sup> which was considered in literature only as a metastable one<sup>18</sup>.

It is rather likely that pressure-induced phase transformations can also occur in hydrogenated multicomponent industrial titanium alloys. However, there were no available data on the high-pressure behavior of such alloys.

## ON THE NATURE OF HYDROGEN IMPROVED WORKABILITY

As concerns the nature of the hydrogen-improved workability, many authors attributed the favorable effect of hydrogen on the mechanical properties to the marked extension of the stability region of the  $\beta$ -phase, thus, to increased content of the  $\beta$ -phase at hot working because the  $\beta$ -phase is assumed to be the most workable one. But there were found several other phenomena which also essentially affect the mechanical properties of hydrogenated titanium alloys. The above discussed thermal pre-strain treatment increases content of the metastable phases in alloys and results in the effect of the transformation plasticity. The hydrostatic component of the stress tensor prevents from nucleation and growth of cracks, which also facilitates the brittle to ductile transition. High hydrogen mobility facilitates relaxation of internal strains by means of stimulated local phase transformations. Besides, hydrogen as alloying element changes properties of the alloy phases. It was shown<sup>12</sup> that hydrogen activated

prismatic and pyramidal dislocation slip systems in the  $\alpha$ -phase as well as in the  $\beta$ -phase. Grain-boundary slip became active over the equicohesive temperature of about 700°C, which resulted in a contribution from normal superplasticity phenomena<sup>19</sup>.

Thus, there are rather many microscopic processes which contribute to result in hydrogen-improved workability. To elucidate all contributions to this beneficial phenomenon, further study of the plastic flow of titanium alloys is necessary both at microscopic and macroscopic levels.

## CONCLUSIONS

1. Hydrogen alloying increases ductility of titanium alloys by 10 to 45 times at moderate temperatures of 400 to 750°C.

2. Hydrogen alloying decreases flow stress by 2 to 3 at optimum.

3. Hydrogen drastically modifies the strain-rate dependence of the stress-strain behavior.

4. Hydrogenation, deformation and dehydrogenation result in a strong grain refinement.

5. Preliminary pre-strain thermal treatment of hydrogenated alloys increases content of the metastable phases and thus markedly increases the alloy ductility.

6. Compacted powder mixtures of titanium and titanium dihydride demonstrate the hydrogen-enhanced plasticity effects on deformation over 500°C, like titanium alloys hydrogenated from the gas phase.

7. Hydrostatic pressure considerably increases workability of hydrogenated titanium alloys. Thus, their ductility at 20–250°C exceeds that of the hydrogen-free alloys in the pressure range of 10 kbar.

8. Phase equilibria in Ti-H alloys are sensitive to pressure. A new phase appears in near-eutectoid alloys at  $P \geq 20$  kbar with a tetragonal structure and hydrogen re-distributed from tetra- to octahedral interstices.

9. These and other hydrogen effects can be useful for improvement of processing of industrial high-strength titanium alloys.

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## **MULTIPLE SCATTERING THEORY AND APPLICATIONS**



## A KKR AND KKR-CPA CODE FOR ANY BRAVAIS LATTICE

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## SOME TECHNICAL PROBLEMS IN KKR CALCULATIONS FOR ANY BRAVAIS LATTICE

The Korringa Kohn Rostoker (KKR) band structure method<sup>1,2</sup>, when compared with other band structure methods, has the advantage of dealing with small matrices due to the fast convergence of scattering operators in angular momentum space. A further advantage is that of dealing with Green's functions. This is particularly valuable in the case of random metallic alloys, where it allows to carry out with relative ease the ensemble configuration averages, necessary in order to evaluate spectral properties. These are performed by various techniques, among which the Coherent Potential Approximation<sup>3</sup> (CPA) has been one of the most successful and reliable approaches<sup>4</sup>. Moreover the algorithm is intrinsically parallel<sup>5</sup> allowing very efficient calculations. There are, of course, a few "bills" to pay. At first the so-called KKR structure constants<sup>6,7</sup>, the empty lattice propagators, are energy dependent and their calculation must be carried out by the Ewald's sums for each energy and k-point. The second shortcoming is that the KKR functions have a pole structure, on the real energy axis, which makes hard the Brillouin Zone (BZ) integration. This usually requires a number of k points for the integration, much larger than other band theory methods.

The most popular and efficient trick to reduce the numerical effort in carrying out the Ewald's sums is due to Stocks et al<sup>8,9</sup>, who separated the structure constants in a regular and an irregular part, by isolating the so called free electron poles. The regular part is a smooth function of k and it can be interpolated by Tchebyshev polynomials. This allowed to perform KKR-CPA calculations in the last fifteen years. In fact, using dimensionless units, the polynomials coefficients do not depend on the lattice parameters for cubic lattices. Moreover, the BZ integration could be performed by "zooming" into the integrand discontinuities<sup>8,9</sup> or by fitting locally the scattering path matrix elements as rational functions of  $k^{10}$ .

The above technique has the practical inconvenience of requiring as many different sets of Tchebyshev coefficients as the unit cell non equivalent sublattices. Furthermore, for non cubic systems, these coefficients depend on the lattice distortion ratios. Namely, for tetragonal lattices different sets of coefficients are required for each value of  $c/a$ . This situation has made difficult the implementation of KKR and KKR-CPA calculations for complex lattice structures as, for example, cuprates.

Regarding the k space integration, various techniques have been implemented specifically for the KKR method. These are different from those used by other band structure methods that employ uniform grids, e.g. the tetrahedron<sup>11</sup> or the special points method<sup>12</sup>. These grids, unfortunately, are quite inefficient for KKR calculations, in which one would like to have a dense grids only in a proximity of the poles. We like to quote here a trick suggested by Zeller<sup>13</sup>, that smoothen out the integrands by a super matrix partitioning designed in order to isolate the free electron poles structure and used in connection with the tetrahedron method.

The most popular KKR BZ integration methods are the so called special directions methods<sup>9</sup>. They consist in decomposing the integral over the irreducible BZ segment into a weighted sum of integrals along radial directions. Line integrals are calculated, say, by fitting the integrand with rational functions. Finally, the integral over the full BZ is obtained by applying the appropriate rotations, according to the crystal symmetry. This method has the advantage of using a not too high number of k points (~1000). However, the resulting grid samples densely the BZ volume near the  $\Gamma$  point but gets much broader near the BZ boundaries. Thus, it might fail when large contributions arise from the BZ edges (e.g. because of Van Hove singularities). Another shortcoming is that it is difficult to estimate its accuracy. This, in fact, turns out not to depend linearly on the total number of k points used. However, this method is a good compromise between accuracy and computing budgets and works well for cubic lattices. A geometrical reason is that the irreducible BZ segments in cubic systems have a pyramidal shape which is quite accurately sampled by radial directions. Unfortunately, this is not the case of most lower symmetry lattices, where the difficulties in using radial directions arise from the little "democracy" of the corresponding directions grid.

We have developed a new KKR-CPA code to deal with any Bravais lattice. This work has required a complete re-thinking of the algorithms used. The main features of the code include: i) Group theory analysis to set up the rotation matrices needed to reduce the integration domain to the irreducible segment. ii) An efficient calculation of the KKR structure constants. iii) A new BZ integration technique able to limit the number of k-points only to those needed for an accurate integration. In this communication we will describe the algorithms we have developed regarding the last two points. About the point (i), although not at all trivial, the reader is referred to basic angular momentum and group theory books<sup>14</sup>.

## OPTIMIZATION OF KKR STRUCTURE CONSTANTS EVALUATION

Following Ham and Segall<sup>6</sup>, the KKR structure constants,  $D_{lm}(\vec{k}, E)$ , can be evaluated as the sum of the three series below (for one atom per unit cell lattices)

$$D_{lm}^{(1)}(\vec{k}, E) = -\frac{4\pi}{v_c} E^{-l/2} e^{E/\eta} \sum_{\vec{g}} \frac{|\vec{g} + \vec{k}|^l e^{-|\vec{g} + \vec{k}|^2/\eta}}{|\vec{g} + \vec{k}|^2 - E} Y_{lm}(\vec{g} + \vec{k}) \quad (1)$$

$$D_{lm}^{(2)}(\vec{k}, E) = -\frac{2}{\pi^{1/2}} (2i)^l E^{-l/2} \sum_{\vec{r}} r^l e^{i\vec{k}\vec{r}} Y_{lm}(\vec{r}) \int_{\sqrt{\eta}/2}^{\infty} dx x^{2l} \exp[-x^2 r^2 + E/(4x^2)] \quad (2)$$

$$D_{lm}^{(3)}(E) = -\frac{\eta^{1/2}}{2\pi} \sum_{s=0}^{\infty} \frac{(E/\eta)^s}{s!(2s-1)} \delta_{l,0} \delta_{m,0} \quad (3).$$

The sums in Eqs. (1) and (2) run, respectively, over the reciprocal space lattice vectors,  $\vec{g}$ , and the real space lattice vectors,  $\vec{r}$  and  $v_c = \vec{a}^3$  is the unit cell volume. The value of the parameter  $\eta$  affects the convergence of both the series (1) and (2). Roughly speaking, increasing  $\eta$  makes slower the convergence of Eq. (1) and faster that of Eq. (2), and vice versa. Our purpose, here, is to find out, for an arbitrary lattice and a given accuracy, the optimal choice,  $\eta_{opt}$ , that minimises the CPU time needed for the evaluation of the KKR structure constants. This choice turns out to depend on the Bravais lattice and the lattice parameters expressed in dimensionless units, on the lattice system, on the energy, on the angular momentum and on the  $\vec{k}$ -vector.

From the analysis of the above formulae, it is evident that the k dependence is reasonably weak. In fact, the quasi-momentum  $\vec{k}$  is involved in Eq. (2) only through a phase factor and does not enter at all in Eq. (3). Moreover,  $|\vec{k}| \ll |\vec{g}|$  for the last contributions to the series (1), and, thus it does not affect seriously the truncation errors. Furthermore, we notice that the truncation errors in the series (1) and (2),  $\mathfrak{R}_l^{(1)}(E, G)$  and  $\mathfrak{R}_l^{(2)}(E, R)$ , as functions of the lengths of the largest vectors included in the reciprocal and direct lattice sums, G and R, do not depend on the azimuthal

quantum number  $m$ . Thus, it is enough to consider here only the  $\bar{k}=0$  case, then, from Eqs. (1) and (2), we have,

$$\Re_l^{(1)}(E, G) \leq \frac{4\pi}{v_c} \eta^{-l/2} \varphi_l(E/\eta) \sum_{|\bar{g}|>G} \frac{g' e^{-g^2/\eta}}{g^2 - |E|} \quad (4),$$

$$\Re_l^{(2)}(E, R) = \frac{2^{\ell+1}}{\pi^{l/2}} \eta^{-l/2} e^{-\text{Re}\{E/\eta\}} \varphi_l(E/\eta) \sum_{|\bar{r}|>R} r^\ell \int_{\sqrt{\eta}/2}^{\infty} dx x^{2\ell} \exp\left[-x^2 r^2 + \text{Re}\{E\}/(4x^2)\right] \quad (5),$$

where we have introduced the functions

$$\varphi_l(x) = e^{\text{Re}\{x\}} |x|^{-l/2} \quad (6)$$

After some manipulations, taking the continuum limit of Eqs. (4) and (5), assuming that

$$G^2 > |E| \quad \text{and} \quad R^2 \eta/4 \gg 1 \quad (7)$$

and using an integral representation of the incomplete gamma function and its asymptotic expansion<sup>15</sup>, we find

$$\Re_l^{(1)}(E, G) \leq \frac{1}{\pi} \varphi_l(E/\eta) \frac{G^2}{G^2 - |E|} \eta^{l/2} \Gamma\left(\frac{\ell+1}{2}, G^2/\eta\right) \quad (8)$$

and

$$\Re_l^{(2)}(E, R) \leq \frac{8\pi^{l/2}}{v_c} \varphi_l(E/\eta) \frac{1}{\eta} \Gamma\left(\frac{\ell+1}{2}, \eta R^2/4\right) \quad (9).$$

As it is apparent from Eqs. (8) and (9), the decay of the errors with the truncation radii in the series (1) and (2) depends only marginally on the energy provided the conditions (7) are verified and it is determined essentially by the incomplete gamma functions. Thus, we can impose both the truncation errors to be as close as possible, simply by equating the arguments of both gamma functions. Thus, putting in Eqs. (8) and (9)

$$\eta R^2/4 = G^2/\eta = p \quad (10),$$

we find

$$\Re_l^{(2)}(E, p, \eta) \equiv \frac{8\pi^{l/2}}{a^3} \varphi_l(E/\eta) \frac{1}{\eta} \Gamma\left(\frac{\ell+1}{2}, p\right) \quad (11)$$

and

$$\Re_l^{(1)}(E, p, \eta) / \Re_l^{(2)}(E, p, \eta) \equiv \left(\frac{\bar{a}}{2} \sqrt{\frac{\eta}{\pi}}\right)^3 \frac{p\eta}{p\eta - |E|} \approx 1, \quad (12).$$

As we shall see the quantity  $p$  will result simply related to the numerical accuracy.

In order to find  $\eta_{\text{opt}}$ , we minimise an expression of the total CPU time,  $T$ , required for the Ewald sums. We assume that  $T$  is proportional to the number of vectors used in both the reciprocal and direct space sums,  $G^3/(2\pi\bar{a})^3$  and  $R^3/\bar{a}^3$ , and to  $t_r$  and  $t_d$  the CPU times required for the evaluation of a single term in each series. In formulae,

$$T = \frac{R^3}{\bar{a}^3} t_d + \frac{N_r G^3}{(2\pi\bar{a})^3} t_r \quad (13),$$

where  $N_r$  is the estimated number of reciprocal space vectors, needed to perform the BZ integration at the given energy E. Eliminating R and G and then minimising with respect to  $\eta$  we easily obtain

$$\eta_{\text{opt}} = \frac{4\pi}{\bar{a}^2} \left( \frac{t_d}{N_r t_r} \right)^{1/3} \quad (14),$$

the corresponding optimal truncation radii for the sums (1) and (2) are

$$G_{\text{opt}} = \sqrt{p \eta_{\text{opt}}} \quad \text{and} \quad R_{\text{opt}} = 2\sqrt{p/\eta_{\text{opt}}} \quad (15).$$

Accordingly, the upper bound for the truncation errors is estimated as the sum of Eqs. (11) and (12) at  $\eta = \eta_{\text{opt}}$ ,

$$\mathcal{R}_{\ell, \text{opt}}(E, p) \cong \frac{2\varphi_{\ell}(\varepsilon)}{\bar{a}\pi^{1/2}(t_d/N_r t_r)^{1/3}} \left( 1 + \frac{(t_d/N_r t_r)^{1/2} p}{p - |\varepsilon|} \right) p^{\frac{\ell-1}{2}} e^{-p} \quad (16)$$

and results to be dependent on p and the dimensionless quantity  $\varepsilon$ ,

$$\varepsilon = E/\eta_{\text{opt}} = E\bar{a}^2(t_d/N_r t_r)^{-1/3}/4\pi \quad (17),$$

that, in turn, is the product of a dimensionless energy times the machine dependent quantity  $(t_d/t_r)^{-1/3}$  and is proportional to  $N_r^{-1/3}$ . Given an input tolerance,  $\Delta$ , the equation

$$\mathcal{R}_{\ell, \text{opt}}(E, p) \cong \Delta \quad (18)$$

can be solved by bracketing with, virtually, no extra computing time. Remarkably, the numerical values found for  $\eta_{\text{opt}}$  for fcc lattices turns out to be very close to those given by Davis<sup>7</sup> when  $t_d/N_r t_r \approx 1$ , as appropriate for constant k search. Since our BZ integration algorithm is a constant energy search,  $N_r \approx 1000$ , in our case the above procedure provides smaller  $\eta_{\text{opt}}$  values.

## AN ADAPTIVE QUADRATURE METHOD FOR BRILLOUIN ZONE INTEGRATION OF KKR FUNCTIONS

Adaptive quadrature methods allow the use of variable integration grids<sup>16</sup>. In our version, that we like to call Zeno's method, after the Greek philosopher, we make line integrals, as described below, by using at least three points: say, the first, the last and the middle point. The integral is then evaluated both by Simpson's and three points trapezoidal rules. If the results coincide within a given input tolerance, the procedure is stopped. Otherwise: i) only (this is the difference from the Romberg's method) another point is inserted in between the first two, the interval is halved and the first, middle and last point shifted appropriately, ii) the above procedure is repeated until convergence is obtained for the current interval, iii) the result is accumulated and the integration continues for the next half-interval. It happens, then, that many function evaluations are required in those small regions where the integrand is rapidly varying and just a few where it is smooth. On top of that the accuracy of the integral is automatically defined through the input tolerance.

According to the above method, we rewrite the integration, in the irreducible BZ segment, in terms of the abscissas, a, b and c, along either the reciprocal lattice primitive vectors or any other convenient set as follows

$$\int_{c_1}^{c_2} dc \int_{b_1(c)}^{b_2(c)} db \int_{a_1(b,c)}^{a_2(b,c)} da f(a, b, c).$$

Since the integration limits, as a function of  $c$  and  $b$ , may present discontinuities, the domain is broken conveniently in order to reduce integration errors and the integral is performed by the above Zeno's method coded as cascade routines. We observe that the  $a$ -integration deals with the  $\delta$ -like contributions from the poles, the resulting step-like functions are integrated over  $b$ , and the  $c$ -integration deals with a smooth function. The hardest part is, of course, the  $a$ -integration and the above algorithm could fail close to the real energy axis ( $\text{Im}\{E\} < 0.01 \text{ Ry}$ ), while it is always very efficient and accurate for step-like discontinuities and smooth functions. In a proximity of the real axis, we use the rational fit method described in the first section only for the  $a$ -integration.

The Zeno's method turns out to be very reliable for pure systems. However, for KKR-CPA calculations there is an inconvenience. In fact the solution of CPA equations must be iterated until self-consistency of the effective scattering amplitude and the scattering path matrix, as evaluated by the BZ integration. The CPA error is proportional to the BZ integral error. In successive iterations, Zeno's method provides different values of the last quantity, all of them within the input tolerance, opposite to the case of fixed grid methods that give a constant error. This fact may give rise to numerical disturbances that increase the number of iterations required, occasionally, and, eventually, lead to a failure in getting convergence. Thus, the BZ integration tolerance must be kept very small. The compromise we accept, for the time being, is to set an integration tolerance not bigger than two orders of magnitude than the CPA tolerance. Unfortunately, the achievement of standard CPA tolerance ( $10^{-6}$ ) sometimes produces a quite high numbers of  $k$ -points, when  $\text{Im}\{E\} < 0.1 \text{ Ry}$ .

We checked successfully the Zeno's method by means of analytic functions and against the special directions method as well. Here, we report in Fig. 1, as an example, the density of states ( $\text{Im}\{E\}=0.001 \text{ Ry}$ ) for  $\text{Cu}_{0.75}\text{Pt}_{0.25}$  fcc random alloy, calculated a) by the special directions method, b) by the Zeno's method and c) by the same method but in a fct lattice with  $c/a=1$ . The last is a quite severe test since the unit cell, of course, coincides with that of the fcc, but the integration domain used is totally different. As the reader can see, the agreement between the three calculation is rewarding. From a careful analysis, around  $E=0.42 \text{ Ry}$ , is visible some disagreement from a) with both b) and c), while these are almost indistinguishable at all the energy points. We have done the same kind of calculations by the Zeno's method for various Bravais lattices (e.g. orthorhombic, trigonal, etc.) and all of them agree impressively with b).

Other good news arise from the following observation. We notice that the fct irreducible segment volume is three times as big as that of the fcc, but the number of function evaluations for each energy point of the calculation c) is never more than twice the corresponding number of the

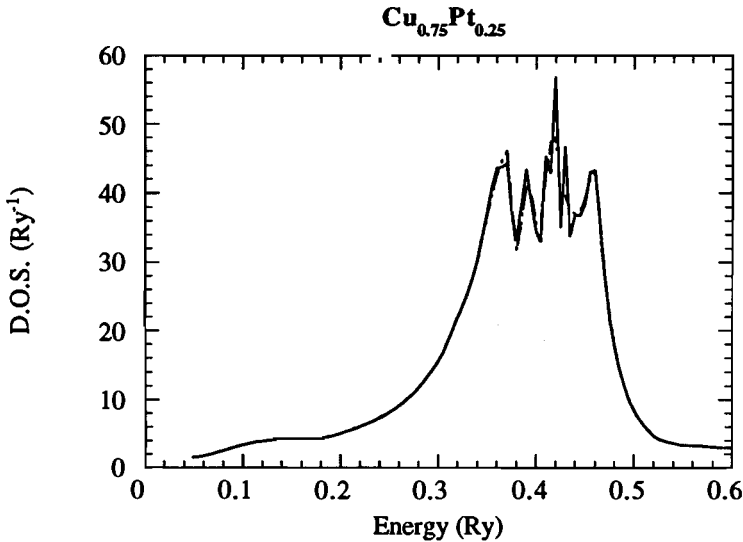


**Figure 1.** Relativistic KKR-CPA D.O.S. for  $\text{Cu}_{0.75}\text{Pt}_{0.25}$  as calculated by a) special directions method (continuous line); b) Zeno's method (long dashed line); c) Zeno's method but in a fct lattice with  $c/a=1$  (dotted line). The site potentials are in the ASA form.

calculation b). The total number of function evaluations, for all the energy spectrum, in turn, is about the same as the special directions method, where it does not depend on the energy, while by the Zeno's method it does. This, of course, is a consequence of the adaptive nature of this new method.

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## FULL MULTIPLE SCATTERING CALCULATIONS ON HgTe UNDER HIGH PRESSURE AT THE MERCURY L<sub>3</sub> X-RAY ABSORPTION EDGE

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### INTRODUCTION

HgTe crystallizes in the zincblende structure at ambient pressure, transforming to a cinnabar structure at 1.5 GPa, at 300K, and then to a rocksalt structure at 8 GPa. Simultaneously to pressure-induced structural changes, transitions from semi-metal -> semiconductor -> metal occur. The zincblende -> cinnabar -> rocksalt transition leads to important changes in the shape of the XANES spectra<sup>1</sup> at the Hg L<sub>3</sub> edge. The goal of these Full Multiple Scattering (FMS) calculations based on a real-space cluster method is threefold : we first want to reproduce the XANES modifications observed under increasing pressure, then confirm the atomic positions determined elsewhere by angular dispersive X-ray diffraction (ADX) and XAS<sup>1,2</sup> by using these data for the construction of the cluster and finally address XANES resonances as fingerprints of the different structures.

# MULTIPLE SCATTERING THEORY APPLIED TO XAS

In a monoelectronic approach, the photoabsorption cross-section can be expressed as :

$$\sigma(E) = 4 \pi^2 \alpha \hbar \omega \sum_{i,f} |\langle f | \vec{e} \cdot \vec{r} | i \rangle|^2 \delta(E_f - E_i - \hbar \omega) \quad (1)$$

where  $\alpha$  is the fine structure constant,  $\hbar\omega$  the photon energy,  $\vec{e} \cdot \vec{r}$  the electric dipole transition operator,  $E_f$  and  $E_i$  the final and initial energy of the monoelectronic states, and  $\delta$  the Dirac distribution. According to the electric dipole selection rules for  $L_3$  edges, a 2p core state photoelectron can be excited towards states with either d or s symmetry. After computation of the radial matrix element, the p to s channel has been found negligible with regards to the p-d channel. The CONTINUUM code developed by Natoli *et al.*<sup>3</sup> has been used to describe the final state wavefunction. This code is based on a real-space cluster method in the muffin-tin framework. The description of the important parameters of these calculations have been given elsewhere<sup>4</sup>. For all the calculations, we have used the same electronic parameters. The final state potential is computed in the so-called "relaxed and screened" potential obtained from the Tl atomic wavefunctions with the configuration : (Xe) 4f<sup>14</sup>5s<sup>2</sup>5p<sup>6</sup>5d<sup>10</sup>6s<sup>2</sup>6p<sup>1</sup>.

## HgTe UNDER INCREASING PRESSURE

The Hg  $L_3$  edges have been measured on the DCI storage ring LURE (France) on the EXAFS dispersive station using a diamond anvil cell<sup>1</sup>. Figure 1(a) shows the top of Hg  $L_3$  edge experimental spectra of HgTe under increasing pressure. The modifications are large in the energy range between 15 to 90 eV. The intensities of some structures increase while other decrease. The total number of features is not even constant.

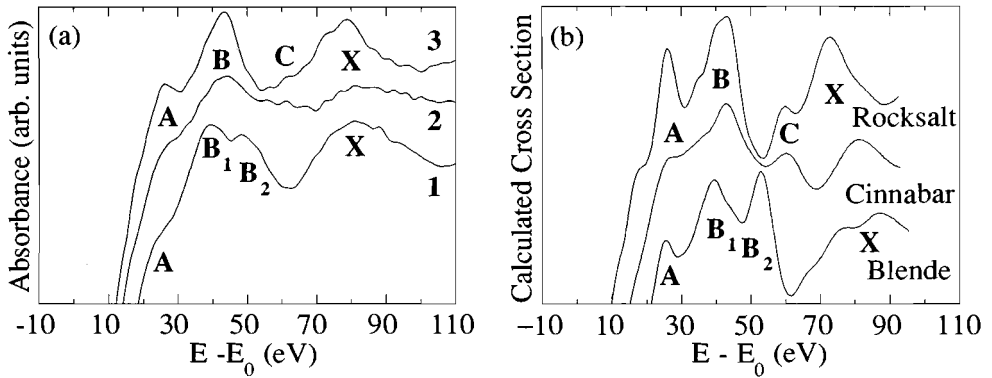


Figure 1 : (a) Experimental Hg  $L_3$ -edge spectra for HgTe : 1 : at 0.2 GPa ; 2 : at 2.8 GPa and 3 : at 10.5 GPa. (b) Calculated Hg  $L_3$ -edge spectra with the structure-type mentioned below each spectrum.



Figure 1(b) presents the results of the FMS calculations for clusters extended to five coordination shells. They have been performed with a complex Dirac-Hara exchange potential<sup>5</sup> which takes into account the inelastic losses suffered by the photoelectron and produces an energy dependent broadening of the calculated structures compared to those obtained with an X- $\alpha$  potential. The atomic positions used to construct the clusters are those determined by ADX<sup>2</sup> and XAS<sup>1</sup> at the L<sub>3</sub> edge of Hg. The cluster sizes necessary to satisfactorily reproduce the experiments are almost the same for the three structures (about 5 to 6 Å in diameter). They are related to the calculated mean-free path of the photoelectron. Despite some discrepancies in the relative intensities of the structures, the agreement between calculated and experimental spectra can be considered as good, in particular the main trends occurring during the phase transition are well reproduced. During the zincblende  $\rightarrow$  cinnabar transition, the shoulder A is shifted towards higher energy and a single structure B appears between B<sub>1</sub> and B<sub>2</sub>. For the cinnabar  $\rightarrow$  rocksalt transition, the features A and B are located at the same energy in both structures but their intensities are enhanced in the NaCl phase.

Figure 2 presents the X- $\alpha$  calculated photoabsorption cross-sections for hypothetical structures at the two critical pressures : at 1.5 GPa, with zincblende and cinnabar structures, and, at 8 GPa, with cinnabar and rocksalt structures. The structural parameters used are extrapolated parameters from the equations of state deduced from experiments<sup>1,2</sup>. The comparison of FMS spectra for the zincblende with P=0.2 or 1.5GPa shows that the energy of the resonance B<sub>2</sub> is not affected by the hydrostatic compression. Feature B<sub>2</sub> is present in an energy range where no resonance is observed on the spectrum of the cinnabar (Fig. 2a) : therefore the resonance B<sub>2</sub> can be considered as a spectroscopic fingerprint of the zincblende phase. All the resonances of the cinnabar phase under pressure (Fig. 2a and 2b) shift to higher energy under increasing pressure as expected for such structural contraction. The comparison of the FMS spectra for the cinnabar and NaCl structures at 8 GPa (Fig. 2b) emphasizes the fact that, from a local point of view, the cinnabar structure may be viewed as a distorted NaCl structure<sup>2</sup> with a large distribution of distances between the Hg absorber and the neighbours. This distribution of distances leads to features smoother for the cinnabar phase than for the rocksalt one but the MS processes involved in both structures are relatively similar. We note for the NaCl structure an intense resonance, labeled C, attributed to a focusing effect involving two shells of atoms collinear with the absorbing atom. Due to the strong forward scattering for any photoelectron energy, the contribution of the fourth mercury shell (at ( $\pm 1$ , 0, 0)) is enhanced by the relay of the first tellurium shell (at ( $\pm 1/2$ , 0, 0)). Consequently, the resonance C can be seen as a characteristic feature of the NaCl type-structure. As expected, this resonance is totally absent in the zincblende spectrum. Finally, the first EXAFS oscillation X undergoes a non monotonous energy shift with pressure : in the transformation from zincblende to cinnabar it goes to higher energy and in the transformation from cinnabar to NaCl is shifted to lower energy. This strange behaviour cannot be predicted by the Natoli's relation<sup>6</sup>. Since the behaviour is nicely reproduced by the calculations, one understands the limitations of phenomenological analysis and the strength of *ab-initio* calculations.

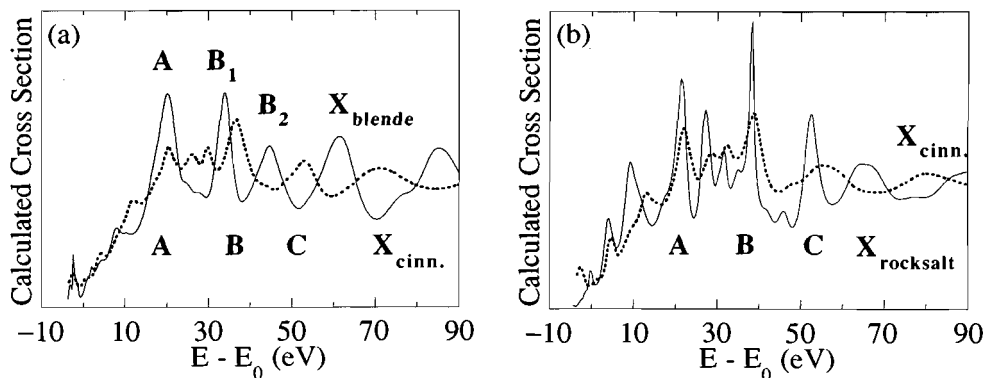


Figure 2 : Calculated Hg L<sub>3</sub>-edge spectra (a) at 1.5 GPa with hypothetical zincblende (full line) and cinnabar (dashed line) structures ; (b) at 8 GPa with hypothetical cinnabar (dashed line) and rocksalt (full line) structures.

## CONCLUSION

The main modifications in the HgTe XANES spectra under pressure are well reproduced only by changing the symmetry around Hg. The good reproducibility proves the accuracy of the atomic positions determined elsewhere. Then the XANES becomes a good test to validate different structural models. This interesting "testing" property is used to determine the phase of HgTe above 12 GPa<sup>7</sup> for which some controversies exist always<sup>8,9</sup>. Finally, some XANES resonances have been addressed as a fingerprint of the structures. This can be helpful to study phase transitions in mercury chalcogenures without translationnal symmetry like liquids.

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## SEMI-RELATIVISTIC MULTIPLE-SCATTERING THEORY

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### INTRODUCTION

Recently, physical phenomena involving the interaction of spin-orbit coupling and magnetism have received much attention (see Ebert and Schütz (1996) for a review). A fully relativistic treatment of these phenomena was proposed in many cases, but a semi-relativistic approach has some advantages. The usual semi-relativistic calculations are done through the Foldy-Wouthuysen transformation. According to Thaller (Thaller 1992, p.311), this procedure is mathematically unsound and gives complicated expressions for the relativistic corrections. On the other hand, Gesztesy, Grosse and Thaller (1984) have proposed a new semi-relativistic expansion of the Green function for the Dirac equation as a compact and convergent series in  $1/c^n$ . Their semi-relativistic expansion was carried out up to  $1/c^2$  to study magnetic circular dichroism in the x-ray range by Brouder, Alouani and Bennemann (1996).

In this paper, we present another application of the semi-relativistic expansion by evaluating the relativistic corrections to the energy up to  $1/c^2$  and  $1/c^4$ . This gives us explicit correction terms to the usual calculation of anisotropy energy in magnetic systems.

### SEMI-RELATIVISTIC EXPANSION OF THE GREEN FUNCTION

The Dirac Hamiltonian for potential  $V$  is

$$H = \begin{pmatrix} V(\mathbf{r}) & cD^\dagger \\ cD & V(\mathbf{r}) - 2mc^2 \end{pmatrix};$$

where each matrix element is a  $2 \times 2$  matrix,  $V$  is a  $2 \times 2$  potential matrix that acts on up and down spins and  $D = -i\hbar\sigma \cdot \nabla$  where  $\sigma = (\sigma_x, \sigma_y, \sigma_z)$  are the Pauli matrices. Compared to the usual Dirac equation, the energy was shifted by  $mc^2$ , so that bound state energies are

negative, as for a non-relativistic Hamiltonian. In most cases,  $D$  is Hermitian ( $D^\dagger = D$ ). For the simplest cases  $V$  is a diagonal matrix, but the formulas are valid when  $V$  is non-diagonal, such as in spiral magnetic structures. The Dirac Green function is the  $4 \times 4$  matrix of operators  $G_D(z) = (z - H)^{-1}$ .

Gesztesy et al. (1984) proved that

$$G_D = \left[ 1 - \begin{pmatrix} 0 & \frac{1}{2mc} G D^\dagger (V - z) \\ 0 & \frac{1}{(2mc)^2} [D G D^\dagger + 2m](V - z) \end{pmatrix} \right]^{-1} \begin{pmatrix} G & \frac{1}{2mc} G D^\dagger \\ \frac{1}{2mc} D G & \frac{1}{(2mc)^2} [D G D^\dagger + 2m] \end{pmatrix} \quad (1)$$

where  $G = (z - H_{NR})^{-1}$  is the  $2 \times 2$  Green function corresponding to the  $2 \times 2$  Hamiltonian  $H_{NR} = \frac{1}{2m} D^\dagger D + V = -\frac{\hbar^2 \Delta}{2m} + V$ . In the case of diagonal  $V$ ,  $G$  is diagonal.

The semi-relativistic expansion is obtained through the identity  $(1 - T)^{-1} = \sum_n T^n$  in Eq.(1). The result is the convergent series

$$G_D = \begin{pmatrix} G & 0 \\ 0 & 0 \end{pmatrix} + \sum_{n=0}^{\infty} \left[ \frac{1}{(2mc)^{2n+1}} \begin{pmatrix} 0 & G D^\dagger Y^n \\ X^n D G & 0 \end{pmatrix} + \frac{1}{(2mc)^{2n+2}} \begin{pmatrix} G D^\dagger (V - z) X^n D G & 0 \\ 0 & [D G D^\dagger + 2m] Y^n \end{pmatrix} \right] \quad (2)$$

where  $X = [D G D^\dagger + 2m](V - z)$  and  $Y = (V - z)[D G D^\dagger + 2m]$ . Such an explicit formula cannot be given by the usual semi-relativistic methods.

In some cases, one is not interested in the Green function but in the Hamiltonian. Grigore, Nenciu and Purice (1989) and Thaller (1992, p.184) gave a formula for the relativistic corrections to the non relativistic eigenstates of energy  $E_0$ . The following discussion is a bit abstract, but it will be illustrated by examples in the next two sections. Equation (2) is rewritten as

$$G_D(z) = \sum_{n=0}^{\infty} \kappa^n G_n(z), \quad (3)$$

with  $\kappa = 1/(2mc)$ . Define the projector  $P(\kappa)$  and its semi-relativistic expansion by

$$P(\kappa) = \frac{1}{2\pi i} \oint_{\Gamma} G_D(z) dz = \sum_{n=0}^{\infty} \kappa^n P_n, \text{ with } P_n = \frac{1}{2\pi i} \oint_{\Gamma} G_n(z) dz, \quad (4)$$

where  $\Gamma$  is a positively oriented contour in the complex plane that isolates the non-relativistic energy  $E_0$  from the other energies of the spectrum. Define also the  $4 \times 4$  non-relativistic projector  $P_0 = P(0)$ . The projector  $P(\kappa)$  projects onto the eigenstates with relativistic energies  $E$  included in contour  $\Gamma$ . In the subspace spanned by the relativistic eigenstates with energies included in  $\Gamma$ , the Hamiltonian is given by

$$P(\kappa) H P(\kappa) = \frac{1}{2\pi i} \oint_{\Gamma} z G_D(z) dz,$$

This formula can be used directly, but to compare with more standard perturbation theory, we can use, for instance, the unitary operator (Kato 1980, p.99)

$$U(\kappa) = [1 - (P(\kappa) - P_0)^2]^{-1/2} [1 - P_0 - P(\kappa) + 2P(\kappa)P_0] \quad (5)$$

that can be used to express the relativistic eigenstates in terms of the non-relativistic ones, because of the intertwining property  $U(\kappa)P_0 = P(\kappa)U(\kappa)$ . The relativistic corrections to the eigenstates of energy  $E_0$  can be obtained by diagonalising the effective Hamiltonian

$$\tilde{H}(\kappa) = E_0 P_0 + \frac{1}{2\pi i} P_0 U(\kappa)^{-1} \oint_{\Gamma} (z - E_0) G_D(z) dz U(\kappa) P_0 \equiv E_0 P_0 + \sum_{n=0}^{\infty} \kappa^n \tilde{H}_n. \quad (6)$$

It is useful to define the intermediate terms

$$\frac{1}{2\pi i} \oint_{\Gamma} (z - E_0) G_D(z) dz = \sum_{n=0}^{\infty} \kappa^n K_n, \text{ with } K_n = \frac{1}{2\pi i} \oint_{\Gamma} (z - E_0) G_n(z) dz, \quad (7)$$

So that  $\tilde{H}_n$  can be expressed in terms of  $P_m$  and  $K_m$ . In the next two sections, we shall carry out this expansion up to  $\kappa^2$  and  $\kappa^4$ .

## SECOND-ORDER $1/c$ EXPANSION

This type of calculation being somewhat unfamiliar, a simple example will be presented in detail. To calculate  $\tilde{H}(\kappa)$ , we expand  $U(\kappa)P_0$  in terms of  $P_n$  in Eq.(6) and multiply by the proper  $K_n$  in Eq.(6).

### Calculation of $\tilde{H}_0$ and $\tilde{H}_1$

We start by showing that  $K_0$  and  $K_1$  are zero, so that expansion (3) starts with  $\kappa^2$ .  $K_0$  and  $K_1$  are the integrals over  $\Gamma$  of  $G_0$  and  $G_1$ . From Eq.(2) we have

$$G_0 = \begin{pmatrix} G & 0 \\ 0 & 0 \end{pmatrix} \quad G_1 = \begin{pmatrix} 0 & GD^\dagger \\ DG & 0 \end{pmatrix}. \quad (8)$$

Using the usual expression for the Green function, we have

$$G(z) = \sum_{m\alpha} \frac{|\psi_m^\alpha\rangle\langle\psi_m^\alpha|}{z - E_m} = \sum_m \frac{p_m}{z - E_m}, \quad (9)$$

where  $p_m = \sum_\alpha |\psi_m^\alpha\rangle\langle\psi_m^\alpha|$  is the projector onto the (eventually degenerate) eigenstates  $|\psi_m^\alpha\rangle$  with energy  $E_m$  of the non relativistic Hamiltonian  $H_{NR}$ .  $|\psi_m^\alpha\rangle$  is a two-component spinor. The projector property  $p_m p_n = \delta_{mn} p_n$  will be often used. From Eq.(9) we find

$$\frac{1}{2\pi i} \oint_{\Gamma} (z - E_0) G(z) dz = \sum_m p_m \frac{1}{2\pi i} \oint_{\Gamma} \frac{(z - E_0) dz}{z - E_m}.$$

According to the Cauchy theorem, the integral is zero if  $E_m \neq E_0$ , because the singularity  $E_m$  is not inside  $\Gamma$ , and it is zero when  $E_m = E_0$  because the singularity of the denominator is compensated by the numerator. Therefore,  $K_0$  and  $K_1$  are zero.

Expansion (6) requires the calculation of  $U(\kappa)P_0$  to zero-th order:  $U(\kappa)P_0 \simeq P_0$ . Using Eqs.(4) and (8),  $P_0$  is obtained from

$$\frac{1}{2\pi i} \oint_{\Gamma} G(z) dz = \sum_m p_m \frac{1}{2\pi i} \oint_{\Gamma} \frac{dz}{z - E_m} = p_0 \quad \text{so that} \quad P_0 = \begin{pmatrix} p_0 & 0 \\ 0 & 0 \end{pmatrix}.$$

This shows that  $P_0$  is indeed the projector onto the non-relativistic eigenstates of energy  $E_0$ . In conclusion,  $\tilde{H}_0 = P_0 K_0 P_0$  and  $\tilde{H}_1 = P_0 K_1 P_0 + P_0 P_1 K_0 P_0 + P_0 K_0 P_1 P_0$ , are zero in Eq.(6).

### Calculation of $\tilde{H}_2$

To calculate  $\tilde{H}(\kappa)$  up to order  $\kappa^2$ , we need only the expansion of  $U(\kappa)P_0$  up to order 0 (i.e.  $P_0$ ) and the term  $K_2$  coming from  $G_2$

$$G_2(z) = \begin{pmatrix} GD^\dagger(V - z)DG & 0 \\ 0 & DGD^\dagger + 2m \end{pmatrix}. \quad (10)$$

From the previous calculation, the only nonzero matrix element of  $K_2$  is

$$\frac{1}{2\pi i} \oint_{\Gamma} (z - E_0) G D^\dagger (V - z) D G dz = \sum_{m,n} p_m \frac{1}{2\pi i} \oint_{\Gamma} \frac{(z - E_0) D^\dagger (V - z) D dz}{(z - E_m)(z - E_n)} p_n.$$

By the residue theorem, the integral is  $D^\dagger (V - E_0) D$  when  $m = n = 0$  and zero otherwise. Finally, the first relativistic correction to the energies and eigenstates corresponding to the non-relativistic energy  $E_0$  is given by  $\tilde{H}(\kappa) \simeq E_0 p_0 + 1/(2mc)^2 p_0 D^\dagger (V - E_0) D p_0$ . In other words, the relativistic corrections are obtained by diagonalising the perturbation matrix

$$\frac{1}{(2mc)^2} \langle \psi_0^\alpha | D^\dagger (V - E_0) D | \psi_0^\beta \rangle = \frac{\hbar^2}{(2mc)^2} \langle \sigma \cdot \nabla \psi_0^\alpha | (V - E_0) | \sigma \cdot \nabla \psi_0^\beta \rangle. \quad (11)$$

This result is remarkably simple as compared to the usual methods. For a spin-polarised potential  $V$ , Kraft, Oppeneer, Antonov and Eschrig (1995) used the elimination method and found the  $\kappa^2$  corrections as a sum of 9 terms, which is equivalent to our Eq.(11). They notice that three terms of their sum have a known physical meaning (spin-orbit, Darwin and mass-velocity corrections), but “the other terms have no special name”.

In the realistic case where the potential is spin-dependent, the “spin-orbit” method is in trouble (should the spin-orbit parameter be calculated with the up or the down spin potential?). The present formalism allows for the use of spin-dependent potential and wavefunctions.

#### FOURTH-ORDER $1/c$ EXPANSION

The calculation of the magnetic anisotropy of non-cubic materials requires an expansion up to  $1/c^4$ . Except in the case of fully relativistic calculations, the expansion is never carried out consistently and only the spin-orbit perturbation is calculated to second order (or to infinite order), without taking account of the other terms of the  $1/c^4$  expansion. In this section, we shall follow Gesztesy et al. (1984) and Grigore et al. (1989) to calculate the terms  $\tilde{H}_3$  and  $\tilde{H}_4$ .  $\tilde{H}_3$  will be found zero and  $\tilde{H}_4$  will give us terms that must be added to the second order spin-orbit calculation to obtain a consistent semi-relativistic expansion.

To obtain  $\tilde{H}(\kappa)$  up to the fourth-order term, we need to expand  $U(\kappa) P_0$  up to second order in Eq.(5):  $U(\kappa) P_0 \simeq P_0 + \kappa P_1 P_0 + \kappa^2 (P_2 P_0 + (1/2) P_1^2 P_0)$ . With the methods of the previous paragraph, we can show that

$$\begin{aligned} P_1 &= \begin{pmatrix} 0 & p_0 D^\dagger \\ D p_0 & 0 \end{pmatrix} & K_2 &= \begin{pmatrix} p_0 D^\dagger (V - E_0) D p_0 & 0 \\ 0 & 0 \end{pmatrix} \\ K_3 &= \begin{pmatrix} 0 & p_0 D^\dagger (V - E_0) D p_0 D^\dagger \\ D p_0 D^\dagger (V - E_0) D p_0 & 0 \end{pmatrix}. \end{aligned}$$

The third-order term is  $\tilde{H}_3 = P_0 K_3 P_0 + P_0 P_1 K_2 P_0 + P_0 K_2 P_1 P_0$ . All the terms of the sum are zero, so that  $\tilde{H}_3 = 0$  (more generally,  $\tilde{H}_n = 0$  for odd  $n$ ).

For the fourth-order term, we need  $P_2$ , which requires the evaluation of

$$I = \frac{1}{2\pi i} \oint_{\Gamma} G D^\dagger (V - z) D G dz = \sum_{m,n} p_m \frac{1}{2\pi i} \oint_{\Gamma} \frac{D^\dagger (V - z) D dz}{(z - E_m)(z - E_n)} p_n,$$

that we split into a sum over  $n \neq m$  and a sum over  $n = m$ . The partial fraction decomposition

$$\begin{aligned} \frac{x - z}{(z - E_m)(z - E_n)} &= \frac{x - E_m}{(E_m - E_n)(z - E_m)} + \frac{x - E_n}{(E_n - E_m)(z - E_n)} \\ \frac{x - z}{(z - E_n)^2} &= \frac{x - E_n}{(z - E_n)^2} - \frac{1}{(z - E_n)} \end{aligned}$$

and the residue theorem yield

$$\begin{aligned} I &= \sum_{n \neq 0} p_0 D^\dagger (V - E_0) D \frac{p_n}{(E_0 - E_n)} + \sum_{m \neq 0} \frac{p_m}{(E_0 - E_m)} D^\dagger (V - E_0) D p_0 - p_0 D^\dagger D p_0 \\ &= p_0 D^\dagger (V - E_0) D G^\perp(E_0) + G^\perp(E_0) D^\dagger (V - E_0) D p_0 - p_0 D^\dagger D p_0, \end{aligned}$$

where  $G^\perp(E_0) = \sum_{n \neq 0} p_n / (E_0 - E_n)$  is the perpendicular Green function, often used in perturbation theory and that has the important property  $p_0 G^\perp(E_0) = G^\perp(E_0) p_0 = 0$ . The fourth order terms are given by the hamiltonian matrix  $\tilde{H}_4 = P_0 K_4 P_0 + P_0 P_1 K_3 P_0 + P_0 K_3 P_1 P_0 + P_0 P_1 K_2 P_1 P_0 + P_0 P_2 K_2 P_0 + P_0 K_2 P_2 P_0 + (1/2) P_0 K_2 P_1^2 P_0 + (1/2) P_0 P_1^2 K_2 P_0$ . Let us call  $Z = p_0 D^\dagger D p_0 D^\dagger (V - E_0) D p_0 + p_0 D^\dagger (V - E_0) D p_0 D^\dagger D p_0$  the sum of the second and third terms. The usual method yields that the fourth term is zero, the sum of the fifth and sixth terms is  $-Z$  and the sum of the seventh and eighth terms is  $Z/2$ . Moreover, the first term is  $P_0 K_4 P_0 = p_0 D^\dagger (V - E_0) D G^\perp(E_0) D^\dagger (V - E_0) D p_0 + 2m p_0 D^\dagger (V - E_0)^2 D p_0 - Z$ . The final result is

$$\begin{aligned} \tilde{H}_4 &= p_0 D^\dagger (V - E_0) D G^\perp(E_0) D^\dagger (V - E_0) D p_0 + 2m p_0 D^\dagger (V - E_0)^2 D p_0 \\ &\quad - (1/2) p_0 D^\dagger D p_0 D^\dagger (V - E_0) D p_0 - (1/2) p_0 D^\dagger (V - E_0) D p_0 D^\dagger D p_0. \end{aligned} \quad (12)$$

For a non-degenerate energy level, this result is identical to the one of Gesztesy et al. (1984), because  $D^\dagger D p_0 = 2m[H_{NR} p_0 - V p_0] = -2m(V - E_0)p_0$ .

For comparison with the usual second-order perturbation in the spin-orbit coupling, we assume that the first order calculation has taken all first-order effects into account as in Eq.(11). The second-order perturbation due to the interaction operator  $W$  is given by

$$E \simeq E_0 + \langle \psi_0 | W | \psi_0 \rangle + \sum_{n \neq 0} \frac{|\langle \psi_n | W | \psi_0 \rangle|^2}{E_0 - E_n} = E_0 + \langle \psi_0 | W | \psi_0 \rangle + \langle \psi_0 | W^\dagger G^\perp(E_0) W | \psi_0 \rangle.$$

Since the first order corrections are represented by the operator  $W = D^\dagger (V - E_0) D$ , the first term of  $\tilde{H}_4$  is the second-order perturbation for  $W$  and the additional terms that must be taken into account to carry out a consistent calculation up to  $1/c^4$  are

$$\begin{aligned} &\frac{2m}{(2mc)^4} \langle D \psi_0^\alpha | (V - E_0)^2 | D \psi_0^\beta \rangle - \frac{1}{2(2mc)^4} \sum_\gamma \langle D \psi_0^\alpha | D \psi_0^\gamma \rangle \langle D \psi_0^\gamma | (V - E_0) | D \psi_0^\beta \rangle - \\ &\frac{1}{2(2mc)^4} \sum_\gamma \langle D \psi_0^\alpha | (V - E_0) | D \psi_0^\gamma \rangle \langle D \psi_0^\gamma | D \psi_0^\beta \rangle \end{aligned} \quad (13)$$

Again, the economy of the method is remarkable. Equation (12) is valid whether energy  $E_0$  is degenerate or non degenerate. For a non-degenerate level, the last two terms are identical and  $\tilde{H}_4$  is the sum of three terms. The equivalent expression obtained by Morrison and Moss (1980) by the Foldy-Wouthuysen method is a sum of eleven terms for a non-magnetic Coulomb potential (for a magnetic one, this number would be at least doubled). Moreover, many of their terms are infinite and “delta function recipies” must be used to find a consistent sum. This is in contrast with the present formula, which is valid even for potentials with Coulomb-type singularities.

## CONCLUSION

The purpose of this paper was to explain the new semi-relativistic expansion and to show how it can be used to carry our explicit calculations in physical cases. The results are simple,

finite and useful, for instance to calculate the magnetic anisotropy of non-cubic systems. For cubic materials, the expansion must be carried out up to  $\tilde{H}_8$ . The power of the present method comes also from its versatility. It can be used to calculate properties of materials with spiral magnetic structure. It can also be extended straightforwardly to current- and spin-density-functional theory (CSDFT). Hjelm, Trygg, Eriksson, Johansson and Wills (1995) and Ebert and Battocletti (1996) have suggested that a correct estimation of orbital magnetisation requires the CSDFT developed by Vignale and Rasolt (1988). The present formalism can be transposed easily to CSDFT. The only change is that  $D$  becomes  $\sigma \cdot (-i\hbar\nabla - q\mathbf{A})$  instead of  $-i\hbar\sigma \cdot \nabla$  where  $\mathbf{A}$  is the self-consistent vector potential. Moreover, several non-relativistic energies can be taken into account together in the perturbation by including them into a common contour  $\Gamma$ .

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# SPIN AND ORBITAL POLARIZED RELATIVISTIC MULTIPLE SCATTERING THEORY

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## INTRODUCTION

Spin polarized band structure calculations for magnetic solids within the framework of local spin density functional theory (LSDFT) that account for the influence of spin-orbit coupling (SOC) got more or less standard during the last ten years. One technique applied for this purpose is to use a scalar relativistic basis set and to account for SOC in the variational step of a conventional  $\vec{k}$ -space band structure method [1]. Alternatively one may solve the Dirac equation for a spin dependent potential [2, 3] and use the solutions as basis functions for a  $\vec{k}$ -space method [4] or within multiple scattering theory [5]. The most prominent shortcoming of both approaches is that they give the orbital magnetic moment induced by SOC up to 60 % too small compared to experiment [5]. The main reason for this is that LSDFT accounts only for spin polarization and therefore supplies even in its present proper relativistic form [6] an insufficient theoretical basis for these kind of band structure calculations. Application of current density functional theory (CDFT) [7, 8] on the other hand should remove these problems. Unfortunately corresponding parameterizations that could successfully be used seem to be not yet available [10]. An alternative to the CDFT approach is the heuristic suggestion by Brooks and coworkers [11, 12, 13] to use a  $\vec{k}$ -space method and to add a so-called orbital polarization (OP) term to the Hamilton matrix. This additional term has been borrowed from atomic theory and is meant to account for Hund's second rule. This approach has been applied with remarkable success to d- as well as f-electron systems and has been refined by various authors [16, 17]. In the following it is shown that Brooks' OP-term can be formulated in a way that can be incorporated into the Dirac equation allowing that way for a corresponding extension of band structure methods based on multiple scattering theory. To demonstrate this, results for the alloy system

bcc-Fe<sub>x</sub>Co<sub>1-x</sub> obtained by the spin and orbital polarized relativistic (SOPR) version of the Korringa-Kohn-Rostoker-Coherent Potential Approximation (KKR-CPA) band structure method for disordered alloys are presented.

## THE ORBITAL POLARIZATION (OP) TERM

For a d-electron system i.e. for the case that orbital magnetism is primarily due to an open d-electron shell, Brooks' OP-term takes the form

$$\Delta\epsilon_{lm_l m_s} = -B_{m_s} \langle \hat{l}_z \rangle_{m_s} m_l \delta_{l2} . \quad (1)$$

This term describes a shift in energy by  $\Delta\epsilon_{lm_l m_s}$  for an orbital with quantum numbers  $l = 2$ ,  $m_l$  and  $m_s$  that is proportional to the average orbital angular momentum  $\langle \hat{l}_z \rangle_{m_s}$  for the  $m_s$ -spin subsystem and the so-called Racah parameters  $B_{m_s}$  that in turn can be represented by the Coulomb integrals  $F_{m_s}^2$  and  $F_{m_s}^4$ . The operator that corresponds to this energy shift is given by

$$\mathcal{H}_{m_s}^{\text{OP}} = -\frac{2}{441} \int \left[ 9 \frac{r^2}{r^3} - 5 \frac{r^4}{r^5} \right] \rho_{dm_s}(r') 4\pi r'^2 dr' \langle \hat{l}_z \rangle_{m_s} \hat{l}_z \delta_{l2} , \quad (2)$$

where  $\rho_{dm_s}$  describes the average charge density of a d-electron with spin character  $m_s$ . It is interesting to note that the operator  $\mathcal{H}_{m_s}^{\text{OP}}$  has the form expected within CDFT for rotational symmetry [8]. This can be seen if  $r \sin \theta \hat{l}_z$  is identified with the  $\phi$ -component of the momentum operator  $\hat{p}$  for spherical coordinates.

The OP-operator in Eq. (2) could be incorporated straightforwardly in the two-component formalism proposed by McLaren and Victora [14] that is obtained by elimination of the minor component in the Dirac equation. Instead of adopting this approach the OP-operator has been further modified appropriately to be used in the four-component Dirac formalism. The symmetry breaking caused by the OP-term is just the same as for the spin dependent part of the exchange-correlation potential [2, 3] giving rise to a coupling of partial waves of the same parity leaving the magnetic quantum number  $\mu$  as a good quantum number. For this reason the extension of the spin polarized relativistic (SPR) version of any band structure method to its SOPR-version can be done in a straightforward way just by modifying the routine that solves the set of coupled radial Dirac equations. In the case of the KKR-band structure method one therefore gets access to the electronic Green's function without any further modifications.

## RESULTS AND DISCUSSION

To demonstrate the application of the above scheme, results obtained using the SOPR-KKR are presented in the following. Fig. 1 gives the orbital magnetic moment as deduced from experiment [15] and calculated using the SPR-KKR (without OP) for pure bcc-Fe, fcc-Co and fcc-Ni. Obviously for Fe and Co the theoretical moments are much too small. Performing LMTO calculations that account for SOC in the variational step and incorporate the OP-term (LMTO-SOC-OP) this discrepancy could more or less be removed. This was demonstrated by Eriksson et al. [16] for the ASA as well as by Trygg et al. [17] for the full potential construction. As can be seen in Fig. 1 using the SOPR-KKR-method one gets nearly the same results. However the great advantage compared to the LMTO-SOC-OP is that one has not to rely on the pseudo-perturbational treatment of SOC. Even more important seems the property that the

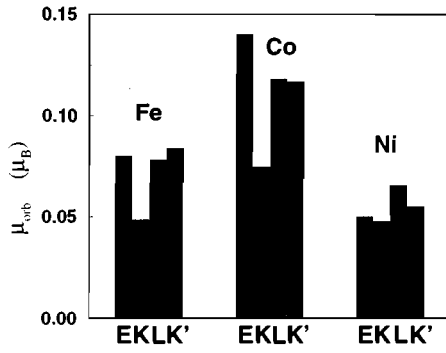


Figure 1: Orbital magnetic moments for bcc-Fe, fcc-Co and fcc-Ni. The columns denoted by E, K, L and K' represent from left to right the experimental data [15] and the theoretical data obtained by the SPR-KKR-, the LMTO-SOC-OP [16] as well as the SOPR-KKR-methods.

SPR-KKR can straightforwardly be combined with the CPA alloy theory to deal with disordered alloys.

The SOC induced orbital magnetic moments  $\mu_{\text{orb}}$  as obtained by the SPR- and SOPR-KKR-CPA for the disordered alloy system bcc-Fe<sub>x</sub>Co<sub>1-x</sub> are given in Fig. 2. As for the pure elements one finds an enhancement of  $\mu_{\text{orb}}$  by the OP-term by around 60 %. This enhancement brings the total theoretical orbital magnetic moment for the alloy in very satisfying agreement with experimental data derived from magneto mechanical as well as spectroscopic g-factor measurements [15].

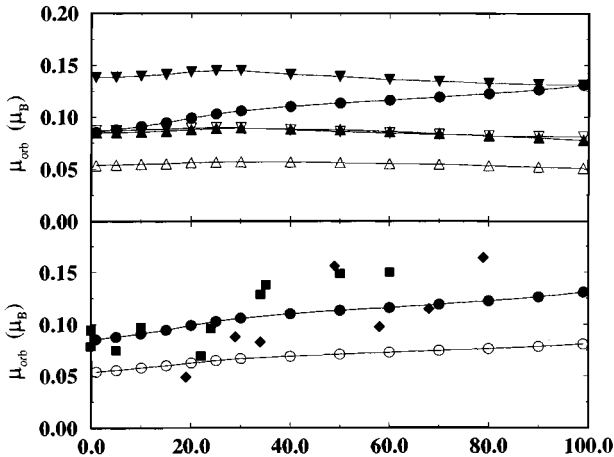


Figure 2: Orbital magnetic moments in bcc-Fe<sub>x</sub>Co<sub>1-x</sub>. The triangles pointing up- and downwards represent the theoretical moments of Fe and Co, respectively, while the concentration weighted sum is given by circles. Full and open symbols stand for results obtained with and without the OP-term included (SOPR- and SPR-KKR-CPA, resp.). Experimental data [15] for the average magnetic moment (bottom) stemming from magneto mechanical and spectroscopic g-factors are given by full squares and diamonds.

The influence of OP on  $\mu_{\text{orb}}$  of  $\text{Fe}_x\text{Co}_{1-x}$  has already been investigated by Söderlind et al. using the virtual crystal approximation (VCA) [18]. Because this simple alloy theory ignores the specific properties of an alloy component by introducing a hypothetical representative atom with a concentration averaged atomic number it led to an incorrect interpretation for the variation of  $\mu_{\text{orb}}$  with concentration  $x$ . As can be seen in Fig. 2 (top)  $\mu_{\text{orb}}$  for Fe and Co are quite different throughout the concentration range. For this reason the variation of  $\mu_{\text{orb}}$  with  $x$  is primarily caused by the varying contributions of Fe and Co, respectively, because of their concentration.

In summary, the OP-term introduced by Brooks and coworkers has been transferred to a corresponding potential term in the Dirac equation. As it is demonstrated this approach allows to account for the enhancement of the spin-orbit induced orbital magnetic moments and related phenomena for ordered alloys as well as disordered systems by a corresponding extension of the SPR-KKR-CPA method.

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## MULTIPLE SCATTERING THEORY APPLIED TO XMCD SPECTRA IN MOLECULE-BASED MAGNETS.

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### INTRODUCTION

Conventional techniques in magnetism measure total magnetic moment (susceptibility measurements by SQUID, Faraday balance). Other more sophisticated techniques such as polarized neutron diffraction can give information on specific groups of atoms but measurements are only possible on large single crystals. X-ray Magnetic Circular Dichroism (XMCD) is a new technique that has recently received a strong interest by the community of magnetism. Magnetic Circular Dichroism has long been known in the energy range of visible light but was not investigated till recently in the X-ray range due to the lack of sources of circular polarized X-rays. The development of Synchrotron Radiation in the last decade impulsed the field of X-ray spectroscopies and XMCD was first observed in 1987.<sup>1,2</sup>

We have studied  $\text{Cs}^{\text{I}}[\text{Ni}^{\text{II}}\text{Cr}^{\text{III}}(\text{CN})_6].2\text{H}_2\text{O}$ , a new type of magnets from inorganic chemistry. This magnet belongs to the family of bimetallic cyanides whose general formulae are  $\text{Cs}^{\text{I}}[\text{A}^{\text{II}}\text{B}^{\text{III}}(\text{CN})_6].n\text{H}_2\text{O}$  where A and B are 3d transition metal ions. These compounds build a new class of insulating magnets that might be good candidates for magneto-optical devices : they have wide gaps, small massic weight and are synthesized at low temperature. They can be easily incorporated into thin plastic films or into paint for industrial applications.

$\text{Cs}^{\text{I}}[\text{Ni}^{\text{II}}\text{Cr}^{\text{III}}(\text{CN})_6].2\text{H}_2\text{O}$  is synthesized through soft chemistry engineering at room temperature.<sup>3,4</sup> A solution of cesium chloride [ $\text{CsCl}$ ] is dropped into a solution of potassium hexacyanochromate  $\text{K}_3[\text{Cr}^{\text{III}}(\text{CN})_6]$  to get the yellow precipitate  $\text{Cs}^{\text{I}}_2\text{K}[\text{Cr}^{\text{III}}(\text{CN})_6]$ . Then a solution of  $\text{Ni}(\text{NO}_3)_2.6\text{H}_2\text{O}$  ( $10^{-2}$  mol in 300 ml) is added dropwise to a 100 ml solution containing an equimolar amount of  $\text{Cs}^{\text{I}}_2\text{K}[\text{Cr}^{\text{III}}(\text{CN})_6]$  that is vigorously stirred up. A light blue precipitate appears and  $\text{Cs}^{\text{I}}[\text{Ni}^{\text{II}}\text{Cr}^{\text{III}}(\text{CN})_6].2\text{H}_2\text{O}$  is collected by centrifugation and then carefully washed with distilled water. The structure of  $\text{Cs}^{\text{I}}[\text{Ni}^{\text{II}}\text{Cr}^{\text{III}}(\text{CN})_6].2\text{H}_2\text{O}$  consists of a three-dimensional assembly of structural motifs  $-\text{N}\equiv\text{C}-\text{Cr}-\text{C}\equiv\text{N}-\text{Ni}-$  where the metallic cations are arranged in a rock salt lattice. The  $\text{Ni}^{\text{II}}$  ions are surrounded by six nitrogen atoms and the  $\text{Cr}^{\text{III}}$  ions by six carbon atoms. Both have an octahedral symmetry. Two water molecules are present per formula unit. Their location although unclear is supposed to be around the  $\text{Cs}^{\text{I}}$  ions.

## X-RAY MAGNETIC CIRCULAR DICHROISM

An XAS experiment is an atomic selective technique that measures the absorption cross section. During the absorption process the atom undergoes a transition from an initial state to a final state and when the absorption cross section is expressed in the electric dipole approximation the interaction Hamiltonian reads  $\vec{\epsilon} \cdot \vec{r}$  where  $\vec{\epsilon}$  is the polarization vector characterizing the photon beam.<sup>5</sup> XMCD is performed when the cross section of a magnetic sample is registered for circularly polarized light. The XMCD signal is the difference between the two cross sections for right and left circularly polarized light.<sup>6</sup>

We have measured X-ray magnetic circular dichroism at chromium and nickel K-edges. In the mono-electronic framework, K-edge corresponds to transitions from the 1s initial state towards p final states above the Fermi level. Contrary to the  $L_{2,3}$  edges, where XMCD signals can be as large as 60 %, the XMCD signals at K-edges is never larger than a few 0.1% of the atomic cross-section. This comes from two facts. Firstly at K-edges there is no spin-orbit coupling acting on the mono-electronic initial state and XMCD finds its origin on the spin-orbit coupling acting on the p levels of the continuum. Secondly the p levels are much less spin polarized than the 3d levels which leads to a smaller contribution to XMCD as can be inferred from recent magnetic sum rules.<sup>7</sup>

The experiments were performed at the energy dispersive absorption beam line of the DCI ring at LURE. In figure 1 we have plotted the XAFS and XMCD signals at the nickel K-edge.

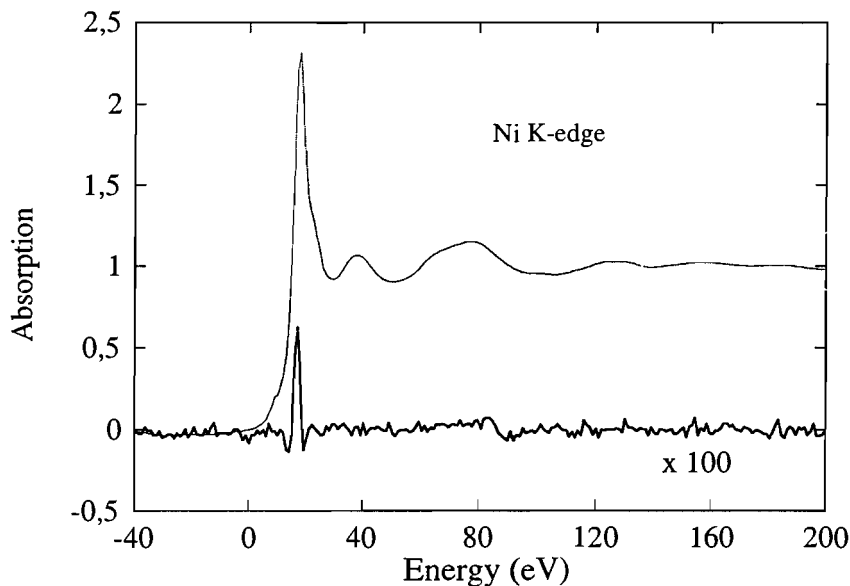


**Figure 1.** Thin line: experimental XAFS at Ni K-edge in  $\text{CsNi}[\text{Cr}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$   
Thick line: experimental XMCD spectra at Ni K-edge in  $\text{CsNi}[\text{Cr}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$

The spectra were recorded with a Si [111] curved polychromator, focusing at 80 cm away between the poles of an electromagnet. The field applied to the sample was larger than 0.5 T and the temperature was 30 K, then insuring a complete saturation of the magnetic moment carried by the magnet. Harmonics were rejected by a silica mirror located before a photo array diode detector. Right circularly polarized photons were selected by positioning a 1 mm wide slit 5.5 mm below the orbit plane. The magnetic field was applied alternatively parallel and anti parallel to the direction of the photon beam. The XMCD signal is the

difference between the anti parallel and parallel polarized spectra normalized by the edge jump of the isotropic spectrum. The energy scale  $E-E_0$  for both chromium and nickel K-edges is relative to the K-edge of the respective pure metallic compound ( $E_0 = 5989$  eV for Cr and  $E_0 = 8333$  eV for Ni). The experimental XAFS and XMCD spectra of chromium have already been plotted elsewhere.<sup>8</sup>

## MULTIPLE SCATTERING APPLIED TO XMCD

The method that we have used derives from the already currently used real space multiple scattering theory applied to XAS.<sup>9</sup> It has been proposed and implemented by Ch. Brouder.<sup>10</sup> One starts from building a cluster of atoms surrounding the absorbing atom. The potential is built in the muffin-tin approximation with a constant potential in the interstitial region. One calculates the Dirac Green function associated to the potential and the cross section is then given by

$$\sigma(\omega) = -4\pi \alpha \hbar \omega \langle i | (\vec{\epsilon}^* \cdot \vec{r}) \text{Im} [G^D(\mathbf{r}, \mathbf{r}'; \kappa)] (\vec{\epsilon} \cdot \vec{r}') | i \rangle$$

with  $|i\rangle$  the core level quadrivector wave function with binding energy  $E_i$  and  $\kappa^2 = \hbar\omega + E_i$ . Since we are dealing with the Dirac Green function, spin-orbit coupling, that is responsible for XMCD, is already present in the expression of  $G^D$ . Brouder proposed to calculate  $\sigma(\omega)$  using a semi-relativistic approach, where the Dirac Green function is given as an expansion at the first order in the Green function for the Pauli Hamiltonian. From this formalism, one ends up with a concise form of the XMCD signal that can be in turn split into three different contributions. Each contribution is the difference between spin up and spin down of rather lengthy expressions that are not given here. The contributions are labeled  $\sigma_{1a}$ ,  $\sigma_{1\ell}$  and  $\sigma_{1n}$ . The index 1 reminds the fact the magnetic cross section originates from development of Dirac Green function at the first order in  $1/c^2$ .  $\sigma_{1a}$  is an atomic only contribution (Fano effect),  $\sigma_{1\ell}$  is roughly proportional to the difference between spin up and spin down density of empty states and  $\sigma_{1n}$  comes mainly from the spin orbit scattering of the photoelectron by the magnetic neighboring sites with also a part of scattering by the potential of the absorbing atom.

This method has already been used successfully for metallic iron.<sup>10</sup> It presents several important advantages. It is a real space calculation for which no translational invariance is required. Calculation up to 500 eV above the edge can be performed because the basis set increases proportionally with the photoelectron energy. The separation between the three contributions ( $\sigma_{1a}$ ,  $\sigma_{1\ell}$  and  $\sigma_{1n}$ ) gives also new insight into the physics that is at the origin of XMCD.

## RESULTS

The muffin-tin potential around each atom in the unit cell has been calculated in the framework of the Local-Spin-Density-Approximation using the ASW method.<sup>11</sup> The ASW method uses the atomic sphere approximation (ASA), i.e. for each atom a sphere radius is chosen such that the sum of the volumes of all the overlapping spheres equals the unit cell volume. The calculation yields the expected ferromagnetic coupling between Cr and Ni. From the self-consistent spin polarized DOS, partial and total magnetic moment per formula unit can be computed. The calculated total magnetic moment is  $5.2 \mu_B$  in agreement with the experimental value ( $5.3 \pm 0.1 \mu_B$ ).<sup>3</sup> All the calculations presented here have been performed on large clusters (225 atom cluster, that is 20 Å in diameter) and cluster size convergence has been checked with larger clusters calculations (681 atoms).

The  $\ell$  expansion has been cut to  $\ell_{\max}=3$  for kinetic energies less than 50 eV and  $\ell_{\max}=4$  for higher kinetic energies and full advantage has been taken from the local point group symmetry of the absorbing atom in building the angular basis set. In figure 2, we report the calculations performed at nickel K-edges and figure 3 represents the superposition of the calculated and the experimental XMCD signals at Cr K-edge.

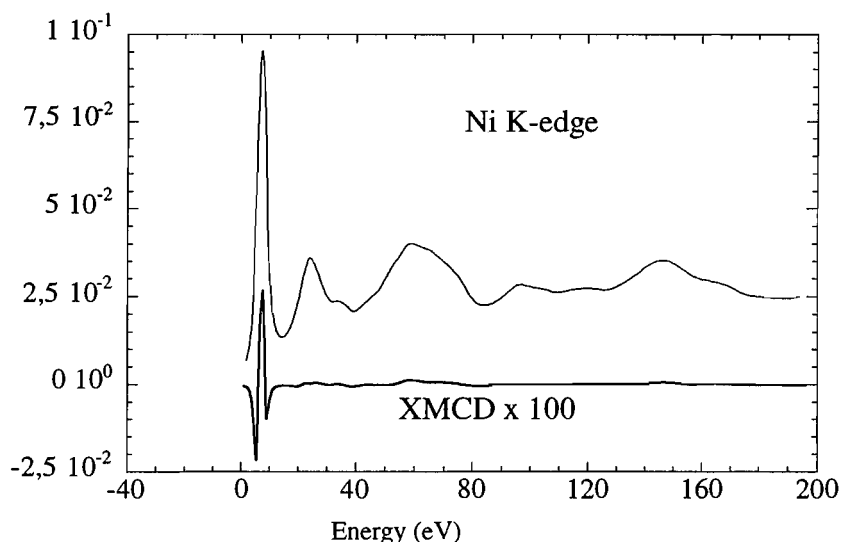


**Figure 2.** Thin line: calculated XAFS at Ni K-edge in  $\text{CsNi}[\text{Cr}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ . Thick line: calculated XMCD spectra at Ni K-edge in  $\text{CsNi}[\text{Cr}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ .

The derivative like signal at the Cr K-edge and the one lobe signal at the Ni K-edge are well reproduced by the calculations. The difference in shape of the two signals come mainly from the fact that the first empty magnetic levels on Ni lie at lower energy compared to the equivalent Cr levels. This is confirmed by calculating at Nickel K-edge the XMCD signal corresponding to "virtual" transitions below the Fermi level. One finds that the negative XMCD lobe lies for Ni K-edge below the Fermi level. The derivative like feature is characteristic of XMCD signal for such compounds: indeed it has also been found in similar molecular based magnets at Vanadium and Manganese K-edges.

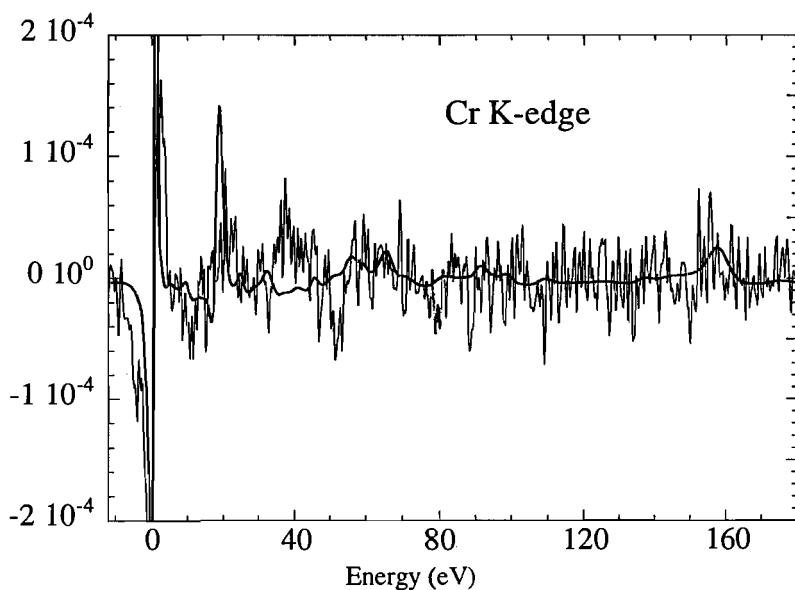


**Figure 3.** Experimental (thin line) and theoretical (thick line) XMCD spectra at Cr K-edge in  $\text{CsNi}[\text{Cr}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ .



In figure 3, we have plotted the XMCD signal in the first 20 eV. Beyond the derivative like feature, one notices a positive resonance at 20 eV and a so called "double-excitation" feature between 40 and 50 eV. Above 50 eV the oscillations are difficult to distinguish from the noise. In the whole energy range between 0 and 200 eV, the theoretical spectrum nicely follow the experiment except for the double excitation.<sup>12</sup>

As mentioned above, one advantage of the method is to allow a decomposition of the different contributions to the total XMCD signal. The theoretical XMCD signals for chromium has been plotted in Figure 4 for two different energy ranges. In the energy range close to the edge (the first 50 eV) the XMCD signal is dominated by  $\sigma_{1n}$  with also a rather large contribution from  $\sigma_{1l}$  (Left panel of Fig.4). This situation is different from the one encountered in metallic iron, where the contribution from  $\sigma_{1n}$  was largely the dominant term close to the edge. This can be understood from the fact that the first neighbors of Cr are Nitrogen and Carbon atoms of the cyano bridge. Although they are spin polarized, they cannot be considered as magnetic neighbors and then only faintly contribute to  $\sigma_{1n}$ . The closest magnetic neighbors are Nickel atoms that are 5 Å away from Chromium atoms. On the other hand in the energy range far from the edge the XMCD signal is mainly dominated by  $\sigma_{1l}$  and XMCD signal is found in phase with the total density of empty states (Right panel of Fig.4).  $\sigma_{1a}$  is the smallest contribution. It has almost no structures and oscillates softly around zero.

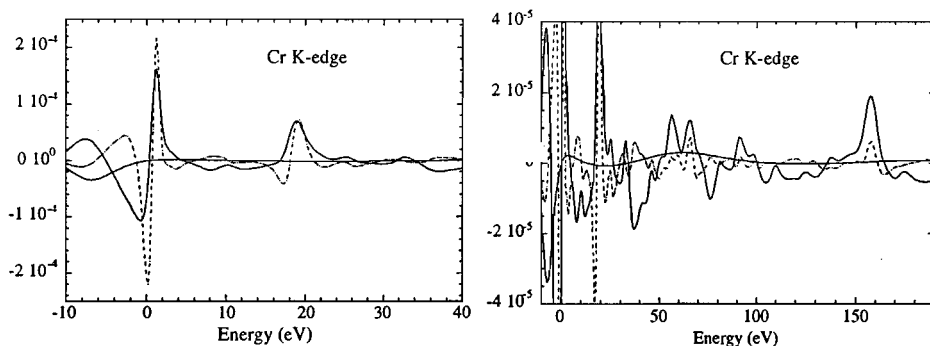


**Figure 4.** Contributions to XMCD.  $\sigma_{1a}$ : thin line;  $\sigma_{1l}$ : thick line;  $\sigma_{1n}$ : broken line. Left panel: XANES; right panel: EXAFS

## CONCLUSION

In this paper we have presented theoretical calculation of XMCD signal in a molecular based magnet. Experiments and theory agree nicely and allow to attribute the origin of the magnetic features present in the XAFS spectrum. Mainly the difference between purely atomic contribution, spin polarized density of states and spin-orbit scattering has been computed. We have shown that purely atomic effects only slightly contribute in the whole energy range. Close to the edge, the spin-orbit scattering dominates over spin polarized density of states while it is the contrary for the magnetic EXAFS.

## ACKNOWLEDGMENTS

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# MULTIPLE SCATTERING THEORY FOR SUBSTITUTIONAL ELECTROMIGRATION

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## INTRODUCTION

The charm of multiple scattering theory in solids is its exact treatment of the scattering of the electrons by the atomic potentials. Examining its development for alloys it becomes clear that a one-to-one correspondence of the scatterers in the alloy and the reference system has ever served as a basic assumption. This holds both for dilute and arbitrary binary alloys, in which systems the commonly used reference systems are the unperturbed host system and the self-consistently constructed coherent-potential system. This assumption breaks down if one wants to describe electromigration in substitutional alloys. A metal atom or an impurity, migrating from its initial lattice position to a neighboring vacancy, has to be described at all positions along the jump path. A notorious position at which no one-to-one correspondence exists is the saddle-point position, halfway. If one thinks in terms of the unperturbed host as a reference system, a cluster of two host atoms has to be used, corresponding to the initial and final positions of the migrating atom.

It will be shown that a more elegant and more easily applicable solution of the problem is given by choosing another reference system. Both the dilute alloy and the unperturbed host can be described with respect to a common reference system, which consists of the unperturbed part of the alloy system and for obvious reasons is called void system. This void system allows for a single-site evaluation of the matrix element describing the wind force in electromigration and the  $t$ -matrix element required for the calculation of the residual resistivity due to a saddle-point defect.

The paper is organized as follows. First the problem will be stated in a historical context. Subsequently, the matrix elements for electromigration and the residual

resistivity will be discussed. Applications of the formalism to electromigration in Al are given in a separate section. The paper ends with a summary and some concluding remarks.

## MODELING OF SCATTERING IN DILUTE ALLOYS

The exact treatment of the scattering of a metal electron by an impurity traces back to the pioneering work of Friedel [1]. Compared to the complete matrix element

$$T_{kk'} = \langle \psi_k^{\text{host}} | V - V^{\text{host}} | \psi_{k'} \rangle = \int d^3r \psi_k^{\text{host}*}(\mathbf{r}) (V(\mathbf{r}) - V^{\text{host}}(\mathbf{r})) \psi_{k'}(\mathbf{r}), \quad (1)$$

in which the state label  $k$  combines the crystal momentum  $\mathbf{k}$  and the band index  $n$ , the model was chosen as simple as possible. The complete configuration is represented schematically in Fig. 1. For the moment we consider only the upper left defect, showing a substitutional impurity with some charge transfer. Moderate lattice distortion can

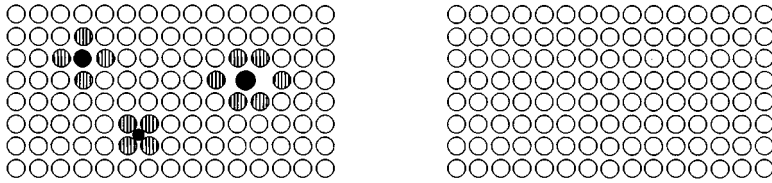


Figure 1: A dilute alloy system, showing a substitutional impurity, an interstitial impurity and an electromigration defect, and its reference system, the unperturbed host system. Some charge transfer effects are shown. Lattice distortion effects are omitted.

be accounted for easily [2], but is omitted for the sake of clarity. The states in Eq. (1) are solutions of the Schrödinger equation for the alloy

$$(p^2 + V)\psi_k = E\psi_k \quad (2)$$

and the host system

$$(p^2 + V^{\text{host}})\psi_k^{\text{host}} = E\psi_k^{\text{host}}. \quad (3)$$

Atomic units, with  $\hbar = 2m = 1$ , are used throughout the text. The state label for the energy  $E_k$  is omitted. The elaborated form of  $T_{kk'}$  is [2]

$$T_{kk'} = -\frac{1}{\sqrt{E}} \sum_{jL} c_{kjL}^{\text{host}*} c_{k'jL} \sin(\delta_L^j - \delta_L^{\text{host}}) e^{i(\delta_L^j - \delta_L^{\text{host}})}, \quad (4)$$

in which the phase shifts  $\delta_L^j$  and  $\delta_L^{\text{host}}$  refer to scattering by an alloy atom at lattice site  $\mathbf{R}_j$  and a host atom respectively, the alloy wave function coefficient  $c_{jkL}$  is an angular momentum expansion coefficient, with  $L = (lm)$ , in the representation

$$\psi_k(\mathbf{r}) \equiv \psi_k(\mathbf{x} + \mathbf{R}_j) = \sum_L c_{kjL} R_L^j(\mathbf{x}), \quad (5)$$

in terms of the local regular solutions of the Schrödinger equation, which in the interstitial constant-potential region are of the form

$$R_L^j(\mathbf{x}) = j_L(\mathbf{x}) - i\kappa t_L^j h_L^+(\mathbf{x}), \quad (6)$$

and  $c_{kjL}^{\text{host}}$  has a similar meaning for the host wave function. In Eq. (6)  $j_L(\mathbf{x})$  is the product of a spherical Bessel function  $j_l(\kappa x)$  and a spherical harmonic  $Y_L(\hat{x})$ ,  $h_L^+(\mathbf{x})$  is a similar product for the spherical Hankel function  $h_l^+(\kappa x)$ ,  $\kappa = \sqrt{E}$  and  $t^j$  is the  $t$  matrix of the alloy potential at  $\mathbf{R}_j$ , given by  $t_l^j = -\frac{1}{\kappa} \sin \delta_l^j e^{i\delta_l^j}$ .

The one-to-one correspondence of alloy and host sites is seen explicitly in Eq. (4). For the moment we now concentrate on the transition probability  $\tau_k^{-1}$ . This quantity is proportional to the density of impurities  $n_s$  and, according to the optical theorem, is given by

$$\tau_k^{-1} = -2n_s \text{Im} T_{kk} = \frac{2n_s}{\kappa} \text{Im} \sum_{jL} c_{kjL}^{\text{host}*} c_{kjL} \sin(\delta_l^j - \delta_l^{\text{host}}) e^{i(\delta_l^j - \delta_l^{\text{host}})}, \quad (7)$$

Friedel used the local perturbation  $V - V^{\text{host}}$  as a model for the scattering potential, reduced it even to one spherically symmetric scatterer and calculated the scattering by free electrons. By that, for the scatterer at the origin labeled by  $j = 0$ ,

$$c_{k0L}^{\text{host}} = c_{k0L} = 4\pi i^l Y_L(\hat{k}) \quad (8)$$

in a system with unit volume, and the transition probability reduces to

$$\tau_k^{-1} = \frac{8\pi n_s}{\kappa} \sum_l (2l+1) \sin^2 \delta_l \quad (9)$$

In spite of its simplicity this approach, supplemented with Blatt's correction [3] for lattice distortion, was applied successfully for decades [4, 5] in studies of systematics in the residual resistivity. Its power was the exact treatment of the scattering and the use of the Friedel sum rule [1] as a self-consistency condition ensuring a correct valency difference between impurity and host atom.

The correct embedment in a metallic host was first accounted for by the Coleridge group [6], which used a single-site simplification of Eq. (7) as a scheme for fitting Dingle temperatures. The embedment gives rise to back scattering of the outgoing scattered waves and results in a difference between alloy and host wave function coefficients. Up to  $l = 2$  this difference is simply given by a diagonal back scattering matrix  $A_L$  and the following relation holds

$$c_{k0L} = A_L c_{k0L}^{\text{host}} \quad (10)$$

by which Eq. (7) obtains the reduced form

$$\tau_k^{-1} = \frac{2n_s}{\kappa} \sum_L |c_{k0L}^{\text{host}}|^2 \text{Im} A_L \sin(\delta_l^0 - \delta_l^{\text{host}}) e^{i(\delta_l^0 - \delta_l^{\text{host}})}. \quad (11)$$

This equation is easily used for fitting. It contains calculated host wave function coefficients and, up to  $l = 2$ , it depends on just three fitting parameters  $\eta_l$ , composed of system parameters as follows

$$\eta_l = \delta_l^0 - \delta_l^{\text{host}} + \theta_l, \quad (12)$$

$\theta_l$  being the phase of the complex number  $A_L$ .

All *ab initio* applications of multiple scattering theory in dilute substitutional alloys rely on the one-to-one correspondence configuration. This holds both for the calculation of transition probabilities [7], represented by Eq. (7), and the electronic structure [8], represented by the Green's function equation [9]

$$\mathcal{G}_{LL'}^{jj'} = \mathcal{G}_{LL'}^{\text{host},jj'} + \sum_{j''L''} \mathcal{G}_{LL''}^{\text{host},jj''} (t_{l''}^{j''} - t_{l''}^{\text{host}}) \mathcal{G}_{L''L'}^{j''j'}, \quad (13)$$

showing that the alloy Green's function matrix  $\mathcal{G}^{jj'}$  follows right away from the host Green's function matrix. The latter is given by the Brillouin zone integral

$$\begin{aligned}\mathcal{G}^{\text{host},jj'} &= \frac{1}{\Omega_{\text{BZ}}} \int_{\text{BZ}} d^3k e^{i\mathbf{k}\cdot\mathbf{R}_{jj'}} b(\mathbf{k}) \frac{1}{1 - t^{\text{host}}b(\mathbf{k})} \\ &= -t^{\text{host}-1} \delta_{jj'} + \frac{t^{\text{host}-1}}{\Omega_{\text{BZ}}} \int_{\text{BZ}} d^3k e^{i\mathbf{k}\cdot\mathbf{R}_{jj'}} M^{-1}(\mathbf{k}) t^{\text{host}-1},\end{aligned}\quad (14)$$

the second equality, containing the Korringa-Kohn-Rostoker (KKR) matrix  $M(\mathbf{k}) \equiv t^{\text{host}-1} - b(\mathbf{k})$ , being valid up to the cut-off angular momentum. That the one-to-one correspondence configuration is used in the coherent-potential approach to binary alloys can be considered as obvious [10]. For such a configuration in dilute alloys some lattice distortion can be included [11, 12].

Extension to interstitial alloys can be accomplished without violating the one-to-one correspondence assumption. All atoms around the interstitial can be related to host lattice positions, see the lower defect in Fig. 1, while the host is treated as having no scatterer in the corresponding interstice. Nevertheless a rather serious problem arises, because the more complicated integral

$$\mathcal{G}^{\text{host},pp'} = \frac{1}{\Omega_{\text{BZ}}} \int_{\text{BZ}} d^3k e^{i\mathbf{k}\cdot\mathbf{R}_{pp'}} [b^{pp'}(\mathbf{k}) + b^{pj}(\mathbf{k}) M^{-1}(\mathbf{k}) b^{p'jT}(-\mathbf{k})], \quad (15)$$

the interstitial host Green's function matrix, has to be evaluated as soon as  $p$  refers to an interstitial position. The  $b$  matrices are defined by

$$b^{pp'}(\mathbf{k}) = \sum_{j'} B(\mathbf{R}_{pp'} + \mathbf{R}_{jj'}) e^{-i\mathbf{k}\cdot(\mathbf{R}_{pp'} + \mathbf{R}_{jj'})}. \quad (16)$$

If the  $p$  labels refer to lattice sites  $j$ , this matrix reduces to  $b(\mathbf{k})$  in the KKR matrix  $M(\mathbf{k})$  and Eq. (15) can be shown to reduce to Eq. (14). The evaluation of  $\mathcal{G}^{\text{host},pp'}$  is hindered by the free-electron poles in the  $b$  matrices. This has formed a barrier for electronic structure calculations of interstitial impurities, but in some cases this problem was bypassed by using an extended lattice in which interstitial atoms occupy a lattice site. For the calculation of Dingle temperatures [13] and interstitial electromigration [14] the accuracy was just sufficient. Recently this accuracy problem has been solved [15, 16].

Now we turn to configurations which are typical for electromigration. In the process of electromigration a diffusive atomic current is induced by an applied voltage, which has been measured for an interstitial such as hydrogen [17, 18], but also for substitutional defects, composed of an impurity or a host atom and a neighboring vacancy. This process has been reviewed recently [19]. Famous is the so-called aluminum catastrophe in integrated-circuit industry, which refers to damage of the electrical contact region due to migration of vacancies towards the cathode. The third defect depicted in Fig. 1 shows an atom on its way to the neighboring vacancy. In order to describe the force on the migrating atom due to the current-carrying electrons, the so-called wind force, it is necessary to calculate the alloy wave function at that atom at all positions along the path. That is because in experiments the work by the driving force is measured. Divided by the path length the average force is the measured quantity.

It is clear that the one-to-one correspondence assumption readily breaks down, notoriously at the position halfway along the path, the saddle point position. This is considered as the most important point apart from the initial position [20, 21], because conventionally the force has been calculated by averaging its values at initial position and saddle point. Until now only the model-pseudopotential method was used, which

is only applicable to simple metals and weak scatterers. No *ab initio* method is fully operative yet [22]. In fact, Landauer [23] considers the field of electromigration as being largely ignored by theoreticians. This is illustrated also by the long-standing controversy concerning the screening of the direct electrostatic part of the driving force. Complete screening [24] and effectively no screening [25] were the two extreme viewpoints. The controversy, which arose in the beginning of the sixties, was clarified only recently [18, 26] and by that hopefully resolved. It can be considered a challenge to see whether the KKR-Green's function method can be adapted to a system of scatterers, that violates the one-to-one correspondence assumption. A formulation for it is already available [27], but in partially applying it this formulation turned out to be hard to handle [22]. The region in the host corresponding to the migrating atoms is treated as a cluster, an old idea already [2], formulated to deal with large lattice distortion, but it has never been applied in practical calculations, apart from finite cluster model treatments [28, 29]. Such a formulation is also cumbersome for electronic structure calculations. In the following section a new, intermediate reference system will be implemented. The results obtained have again the one-to-one correspondence form and the way seems free also for self-consistent electronic structure calculations.

## THE MATRIX ELEMENTS VIA THE VOID SYSTEM

The matrix elements of interest are

$$M_k^{\text{wind}} = \langle \psi_k | -\nabla_{\mathbf{R}_p} v_p | \psi_k \rangle, \quad (17)$$

occurring in the expression for the wind force [21] on the atom with potential  $v_p$  located at the alloy position  $\mathbf{R}_p$ ,

$$\mathbf{F}_p^{\text{wind}} = \sum_k \delta f(k) \langle \psi_k | -\nabla_{\mathbf{R}_p} v_p | \psi_k \rangle, \quad (18)$$

and the scattering matrix element  $T_{kk'}$  given by Eq. (1). The deviation  $\delta f(k)$  from  $f_0(E_k)$ , the equilibrium Fermi-Dirac distribution function, due to the applied electric field  $\mathbf{E}$ , is given by

$$\delta f(k) = e\tau_k^{\text{tr}} \mathbf{E} \cdot \mathbf{v}_k df_0(E_k)/dE_k, \quad (19)$$

where  $\tau_k^{\text{tr}}$  is the  $k$  dependent transport relaxation time of the electron,  $e$  is its charge and  $\mathbf{v}_k$  is its velocity.

Looking at the two matrix elements  $M_k^{\text{wind}}$  and  $T_{kk'}$  one has to solve two problems regarding the break down of the one-to-one correspondence assumption. For both matrix elements the alloy wave function  $\psi_k(\mathbf{r})$  is required, which is a solution of Eq. (2) and is centered at alloy positions. The perturbed part of the alloy potential  $V$  is denoted by  $V_c$  and given by

$$V_c = \sum_p v_p \quad (20)$$

Provided this problem is solved and the alloy wave function has become available, the matrix element  $M_k^{\text{wind}}$  can be evaluated straightforwardly, because the potential in it is centered at an alloy position. One is faced with an additional problem in evaluating  $T_{kk'}$ . The host atoms in  $V_c^{\text{host}} = \sum_j v_j^{\text{host}}$  are centered at unperturbed lattice sites. The same holds for the host wave function, to be found by solving Eq. (3) using an expansion which is similar to Eq. (5). So the spatial  $T_{kk'}$  - integral involved, see Eqs. (1)

and (20), can not be evaluated using multiple-scattering-theory methods developed up to now, because all of them rely on the one-to-one correspondence of  $p$  and  $j$  labels. We will show that both problems can be solved by introducing an auxiliary void reference system, depicted schematically in Fig. 2.

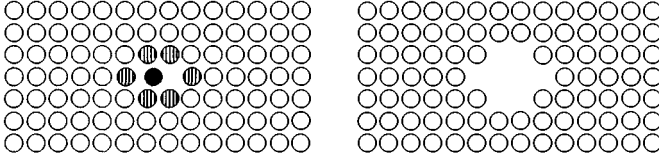


Figure 2: The defect corresponding to a migrating atom in a dilute substitutional alloy and the corresponding void reference system.

The basic equations to be used are the Lippmann-Schwinger equations for the alloy wave function

$$\psi_k = \psi_k^{\text{void}} + G^{\text{void}} \sum_p v_p \psi_k, \quad (21)$$

the host wave function

$$\psi_k^{\text{host}} = \psi_k^{\text{void}} + G^{\text{void}} \sum_j v_j^{\text{host}} \psi_k^{\text{host}}, \quad (22)$$

the Green's function of the alloy

$$G = G^{\text{void}} + G^{\text{void}} \sum_p v_p G \quad (23)$$

and of the host

$$G^{\text{host}} = G^{\text{void}} + G^{\text{void}} \sum_j v_j^{\text{host}} G^{\text{host}}, \quad (24)$$

described with respect to the void system. For the void Green's function the following expansion can be written down

$$\begin{aligned} G^{\text{void}}(\mathbf{x} + \mathbf{R}_n, \mathbf{x}' + \mathbf{R}_{n'}) &= -i\kappa \sum_L j_L(\mathbf{x}_<) h_L^\dagger(\mathbf{x}_>) \delta_{nn'} \\ &+ \sum_{LL'} j_L(\mathbf{x}) \mathcal{G}_{LL'}^{\text{void}, nn'} j_{L'}(\mathbf{x}'), \end{aligned} \quad (25)$$

which is valid in the void region. A position label  $n$  is used, which can refer to either an alloy position  $p$  or a host position  $j$ , because both possibilities show up. By solving Eq. (24) in the position representation the matrix  $\mathcal{G}^{\text{void}}$  for host positions appears to be related to the host Green's function matrix, Eq. (14), as

$$\mathcal{G}^{\text{void}} = \mathcal{G}^{\text{host}} (1 + t^{\text{host}} \mathcal{G}^{\text{host}})^{-1} = \mathcal{G}^{\text{host}} - \mathcal{G}^{\text{host}} (t^{\text{host}} + \mathcal{G}^{\text{host}})^{-1} \mathcal{G}^{\text{host}}. \quad (26)$$

The second equality can be used to find  $\mathcal{G}^{\text{void}}$  for arbitrary positions [30],

$$\mathcal{G}^{\text{void}, nn'} = \mathcal{G}^{\text{host}, nn'} - \sum_{jj'} \mathcal{G}^{\text{host}, nj} (t^{\text{host}} + \mathcal{G}^{\text{host}})_{jj'}^{-1} \mathcal{G}^{\text{host}, j'n'}, \quad (27)$$



in which the generalized host Green's function matrix has the form of Eq. (15).

The relations between the alloy and the host wave function coefficients to the void wave function coefficients,

$$c_k = c_k^{\text{void}} + \mathcal{G}^{\text{void}} t c_k \text{ and } c_k^{\text{host}} = c_k^{\text{void}} + \mathcal{G}^{\text{void}} t^{\text{host}} c_k^{\text{host}}, \quad (28)$$

are found by solving Eqs. (21) and (22), respectively. The void wave function coefficients  $c_{kpL}^{\text{void}}$  in the alloy equation are related to  $c_{kjL}^{\text{void}}$  in the second equation by

$$c_{kpL}^{\text{void}} = \sum_{L'} c_{kjL'}^{\text{void}} J_{L'L}^{jp}. \quad (29)$$

The matrix  $J$  reduces to a Kronecker  $\delta$  in the angular momentum labels for  $p = j$ . The host wave function coefficients being known, the alloy wave function coefficients can now be calculated. The result for  $M_k^{\text{wind}}$  is [27]

$$M_k^{\text{wind}} = -2\kappa \text{Re} \sum_L \sum_{m_1=-(l+1)}^{l+1} c_{kpL}^* \mathbf{D}_{L,l+1,m_1} (t_{l+1} - t_l^* + 2i\kappa t_{l+1} t_l^*) c_{kpl+1,m_1}, \quad (30)$$

in which the vectorial matrix  $\mathbf{D}$  is defined as

$$\mathbf{D}_{LL'} = \int d\hat{x} Y_L(\hat{x}) \hat{x} Y_{L'}(\hat{x}). \quad (31)$$

We now concentrate on the scattering matrix element  $T_{kk'}$  of Eq. (1). The way out of the problem of evaluating it starts with splitting Eq. (1) into two terms,

$$T_{kk'} = \langle \psi_k^{\text{host}} | V_c | \psi_{k'} \rangle - \langle \psi_k^{\text{host}} | V_c^{\text{host}} | \psi_{k'} \rangle. \quad (32)$$

Subsequently Eq. (22) is substituted into the first term and Eq. (21) into the second term,

$$\begin{aligned} T_{kk'} = & \langle \psi_k^{\text{void}} | V_c | \psi_{k'} \rangle - \langle \psi_k^{\text{host}} | V_c^{\text{host}} | \psi_{k'}^{\text{void}} \rangle \\ & + \langle \psi_k^{\text{host}} | V_c^{\text{host}} G^{\text{void}\dagger} V_c | \psi_{k'} \rangle - \langle \psi_k^{\text{host}} | V_c^{\text{host}} G^{\text{void}} V_c | \psi_{k'} \rangle. \end{aligned} \quad (33)$$

The first two terms can be evaluated right away, because the exact states  $\psi_{k'}$  and  $\psi_k^{\text{host}}$  are coupled by their full potentials,  $V_c$  and  $V_c^{\text{host}}$  respectively, to unperturbed *free space* void states. The two other terms are seen to become evaluable after combining them. In the difference  $G^{\text{void}\dagger} - G^{\text{void}}$  the singular part in  $G^{\text{void}}$  precisely cancels. Using  $G^{\text{void}}$  in the position representation, Eq. (25), one finds for the difference of the singular parts  $2i\kappa \sum_L j_L(\mathbf{x}) j_L(\mathbf{x}') \delta_{nn'}$ . By this the problem in evaluating  $T_{kk'}$  is solved. The final expression is

$$\begin{aligned} T_{kk'} = & \sum_{pLL'} c_{kjL'}^{\text{void}*} J_{L'L}^{jp} t_l^p c_{k'pL} - \sum_{jLL'} c_{kjL}^{\text{host}*} t_l^{\text{host}*} J_{LL'}^{jp} c_{k'pL}^{\text{void}} \\ & + \sum_{jp'LL'L''} c_{kjL}^{\text{host}*} t_l^{\text{host}*} [(G_{LL''}^{\text{void},jj*} + i\kappa \delta_{jj'} \delta_{LL''}) J_{L''L'}^{j'p'} \\ & - J_{LL''}^{jp} (G_{L'L'}^{\text{void},pp'} - i\kappa \delta_{pp'} \delta_{L'L'})] t_{l'}^{p'} c_{k'p'L'}. \end{aligned} \quad (34)$$

The infinite internal summations over the angular momentum in connection with the  $J$  matrices can be carried out exactly, just inducing a change of position label as it

is illustrated for the void wave function coefficients by Eq. (29). Expression (34) indeed has a one-to-one correspondence form in the sense, that only  $t$  matrices occur corresponding to atomic scatterers at alloy and host sites. No cluster  $t$  matrices are involved [2]. One just needs the void Green's function matrix with various position labels and the wave function coefficients, but that does not form a problem [30]. For the simple  $p = j$  case Eq. (34) should reduce to Eq. (4). After eliminating  $c_k^{\text{void}}$  with the help of Eq. (28), one indeed finds that

$$T_{kk'} = \sum_{jL} c_{kjL}^{\text{host}*} (t_l^j - t_l^{\text{host}*} + 2i\kappa t_l^{\text{host}*} t_l^j) c_{k'L} \tag{35}$$

which is equivalent to Eq. (4) due to the equality

$$t_l^j - t_l^{\text{host}*} + 2i\kappa t_l^{\text{host}*} t_l^j = -\frac{1}{\kappa} \sin(\delta_l^j - \delta_l^{\text{host}}) e^{i(\delta_l^j - \delta_l^{\text{host}})}. \tag{36}$$

We conclude this section by giving the equation for the alloy Green's function matrix, which is relevant for electronic structure calculations. Elaborating Eq. (23) one finds

$$\mathcal{G} = \mathcal{G}^{\text{void}} + \mathcal{G}^{\text{void}} t \mathcal{G}, \tag{37}$$

in which alloy position labels are suppressed. The matrix  $\mathcal{G}^{\text{void},pp'}$  can be calculated according to Eq. (27). In order to obtain  $\mathcal{G}$  a matrix inversion is required. We want to stipulate that in the present description lattice distortion is accounted for automatically, because the alloy positions can be chosen freely in the void region. It is incorporated in the generalized  $b$  matrix, Eq. (16). For the cases treated up to now the one-to-one correspondence of the alloy to the reference system applied [9, 12]. Eliminating for that  $p = j$  case  $\mathcal{G}^{\text{void}}$  from Eqs. (37) and (26), one finds the reduction to Eq. (13).

Finally we want to remark, that the theory presented applies for non-spherical potentials as well. Explicit expressions such as in Eq. (4) are replaced by expressions in terms of  $t$  matrices, which are non-diagonal in the angular momentum. Matrix expressions such as Eqs. (27) and (28) remain unchanged.

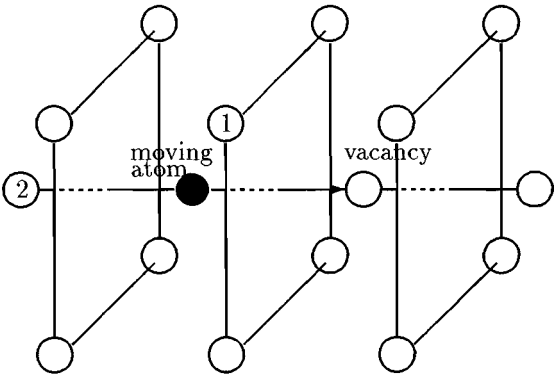


Figure 3: A perspective of the atomic postions around the migration path, running from the moving atom to the vacancy. In some calculations an impurity is located at positions 1 or 2.

# APPLICATIONS

The formalism described above will be used to calculate the wind valence in different systems. The wind force on an atom is proportional to the applied electric field

$$\mathbf{F}^{\text{wind}} = Z^{\text{wind}} e \mathbf{E}. \tag{38}$$

The wind valence  $Z^{\text{wind}}$  is calculated using Eqs. (18) and (17), the latter being given in a more explicit form in Eq. (30). As already mentioned in Sec. , it is necessary to calculate the wind valence at each point along the jump path and to average over the path. We concentrate on wind valences in aluminum host, because of its technological importance. A more microscopic knowledge of the process may help to understand and prevent electromigration-induced damage to occur. One of the successful practical attempts to slow down the damaging effect is the addition of impurities like copper. The wind valence of copper in aluminum will be calculated, as well as the wind valence of an aluminum atom. The influence on the latter quantity of a Cu atom, occupying one of the positions near the path, will be shown also. The jump path and its nearest surrounding atomic positions are depicted in Fig. 3.

Results are displayed in Fig. 4. The wind valence of Al along the path is given by the thick solid line. It is smaller that the wind valence of Cu in Al (thin solid line),

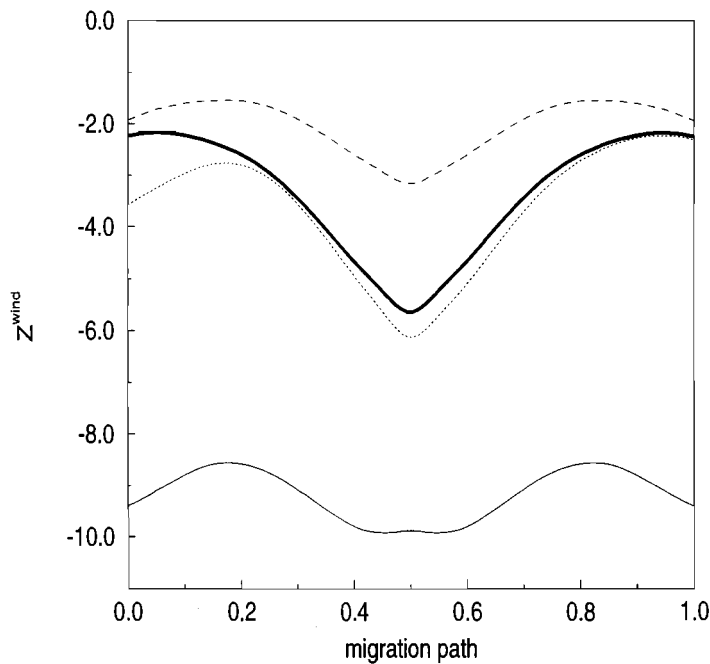


Figure 4: The wind valence in Al along the migration path. The initial and saddle point positions are at the origin and at 0.5 respectively. The lower curve is for Cu, the upper curves are for self-electromigration. The dashed and the dotted curve show the influence of a Cu atom at positions 1 and 2 of Fig. 3 respectively, on the wind force in pure Al (thick curve).

which does not agree with experiment. This may be due to the fact that in practise the diffusion takes place along grain boundaries, while this calculation has been done for bulk metal. The dashed and dotted curves give the wind valence along the path of an Al atom, while one of the surrounding host atoms is replaced by a Cu atom. A Cu atom at the site labeled by 1 in Fig. gives the dashed curve, while one at site 2 gives the dotted curve. The latter curve is not symmetric around the saddle point, which reflects the fact that position 2 is a non-symmetric one. Furthermore the presence of the Cu atom does not diminish the wind valence of Al in all positions. We conclude that quenching of the damaging electromigration cannot be due to the presence of Cu near a migrating host atom in the bulk.

## SUMMARY AND CONCLUSIONS

Defect configurations in dilute alloys, studied up to now in the framework of multiple scattering theory, are such that a one-to-one correspondence exists between the atoms in the alloy and the reference system, the latter system regularly being the unperturbed host system. This one-to-one correspondence does not apply to the defect studied in substitutional electromigration, in which a host atom or an impurity can move to a neighbouring vacancy.

This problem has been solved without using a cluster description of the perturbed region in the dilute alloy [27], which in practice appears to be rather heavy [22]. It has been achieved by taking advantage of an intermediate reference system, the so-called void system, which is built up out of all unperturbed atoms in the alloy. In the void system the defect region is just empty. Both the host system and the alloy are described with respect to the void system. By giving the expression for the matrix element required for the wind force all problems in describing substitutional electromigration are solved. The formalism is applied to electromigration in aluminum. The influence of a Cu atom near a migrating Al atom is also shown.

In addition it has become possible to calculate the scattering of electrons by a defect, in which the migrating atom is halfway along its jump path. Possible applications include the contributions to the residual resistivity of a saddle-point defect and the corresponding universal conductance fluctuations. Finally, the alloy Green's function matrix, required for electronic structure calculations, is given as well. Therefore, everything is ready now for self-consistent calculations of the electronic structure of such defects. Moreover, the method is applicable to configurations at surfaces and in amorphous systems, which could not be treated up to now.

The result of this work can be considered as another illustration of the powerful flexibility of multiple scattering theory with respect to the choice of a reference system [31].

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# THE CHARGE ON A SINGLE IMPURITY IN A METAL

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## ABSTRACT

The techniques for calculating the electronic states of an impurity in a metal from first principles are well understood and have already been implemented. An approximate method that leads to much simpler calculations has been proposed recently. We investigate this method within the framework of the quadratic Korringa-Kohn-Rostoker formalism, and show that it produces surprisingly good predictions for the charge on the impurity.

## INTRODUCTION

When one of the atoms in a metallic crystal is replaced by an atom of a different kind, the electronic charge distribution is changed in the neighborhood. The change in the electronic structure due to an impurity is of interest in many solid state physics applications, and theoretical techniques have been developed to calculate it. The simplest approximation is to assume that the one-electron potential function for the pure metal is modified only in the cell that contains the impurity atom, but it was recognized many years ago that this approach would never give the correct solution because the charge that moves in or out of that cell will of necessity lead to changes in the charges of the neighboring cells. For this reason, in modern calculations<sup>1</sup> the problem is treated

by considering not only the impurity atom but the atoms on several adjoining nearest neighbor shells as a cluster of impurities to be embedded in the host lattice. A proposal was recently made by Johnson and Pinski in connection with alloy theory<sup>2</sup> that leads to an algorithm for calculating the change in the electronic states of an impurity, in an approximate way, without dealing directly with the changes on the neighboring atoms. Some questions have been raised about the applicability of the Johnson-Pinski method in alloy theory<sup>3</sup>, but, in a calculation by R. Zeller that was quoted in ref. 2, it gave promising results for an impurity. In this paper, we carry out other impurity calculations with the Johnson-Pinski method. We show that it is particularly easy to implement using a technique that we have proposed for impurity calculations<sup>4</sup> that is based on the quadratic Korringa-Kohn-Rostoker (QKKR) method for band theory calculations<sup>5</sup>.

## BRIEF REVIEW OF PRESENT METHOD

The Johnson-Pinski method can be justified using the results of first-principles calculations which show that the net charge  $Q_i$  in the impurity cell is almost completely screened by charge transferred to or from the atoms on the nearest neighbor shell. Assuming that the effect of the screening charge can be simulated by a shell of charge at the distance of the nearest neighbor shell, the potential of the impurity atom will experience an electrostatic shift  $\delta V_i$  given by

$$\delta V_i = -\frac{Q_i}{R_1} \quad (1)$$

where  $R_1$  is the distance from a nearest-neighbor to the impurity site. The method is implemented in a self-consistent way by creating an impurity potential  $v_i(\mathbf{r})$  which is placed in the impurity cell with host potentials  $v(\mathbf{r})$  in all the other cells in the crystal. A series of calculations are carried out with shifted potentials  $v_i(\mathbf{r}) + \Delta\sigma_i(\mathbf{r})$ , where  $\sigma_i(\mathbf{r})$  is a step function that is one when  $\mathbf{r}$  is in the impurity cell and zero otherwise and  $\Delta$  is a constant. A net charge within the impurity cell,  $Q(\Delta)$ , will be obtained for each value of  $\Delta$ . When the shift calculated from eqn.(1) with a charge  $Q(\Delta)$  is equal to the shift  $\Delta$  that was used to calculate that charge, self consistency has been achieved. Similar methods have been proposed before<sup>6</sup>.

In principle, the application of this proposal could be difficult because shifting a potential by  $\Delta\sigma_i(\mathbf{r})$  is not a simple thing to do. Normally, it would be necessary to make additional approximations in order to implement it such as replacing the polygonal impurity cell by a sphere. The QKKR method uses scattering matrices that are not diagonal in the angular momentum indices in order to treat scattering from non-spherical potentials. In the band theory application of the method, the equations of Korringa<sup>7</sup>, Kohn and Rostoker<sup>8</sup> are rewritten so that the structure constants are independent of energy by adding an energy dependent shift times a step function  $(E - E_0)\sigma(\mathbf{r})$  to the potential function in each cell in the crystal. The addition of an another shift which is a constant times the step function to the impurity potential is therefore extremely simple.

We have carried out impurity calculations for a zinc atom embedded in a copper matrix. We first perform self consistent band theory calculations on pure Cu and Zn on fcc lattices with the lattice constant of pure Cu, 6.76 Bohr radii. This yields Fermi energies, self consistent potentials, scattering matrices, and wave functions for both metals. The Green's function for a system with a Zn atom embedded in a Cu matrix

can be constructed from these functions using the formulas in ref. 4. The addition of a shift  $\Delta\sigma_i(\mathbf{r})$  to the Zn potential can easily be incorporated into the method, and the resulting Green's function  $G^\Delta(E, \mathbf{r}, \mathbf{r}')$  can be used to calculate the net charge on the impurity site  $Q(\Delta)$  by integrating over the impurity cell and energy

$$Q(\Delta) = -\frac{1}{\pi} \text{Im} \int_{E_0}^{E_F} dE \int_{\text{impur.cell}} G^\Delta(E, \mathbf{r}, \mathbf{r}) d\mathbf{r} - Z_i \tag{2}$$

The Fermi energy,  $E_F$ , of pure Cu is used in this equation,  $Z_i$  is the charge on the impurity nucleus and  $E_0$  is the bottom of the conduction band.

## RESULTS AND DISCUSSION

The charges  $Q(\Delta)$ , obtained according to eqn.(2), are plotted against  $\Delta$  for Zn in Cu in Fig. 1 (dashed line). The straight solid line in that figure is a plot of the charge  $Q_i$  versus the Coulomb shift  $\delta V_i$  that is calculated using eqn.(1). The intersection of these two lines gives the self consistent charge in the Zn impurity cell, which we predict to be a loss of 0.182 electronic charges in very good agreement with other reported results as shown in Table 1.

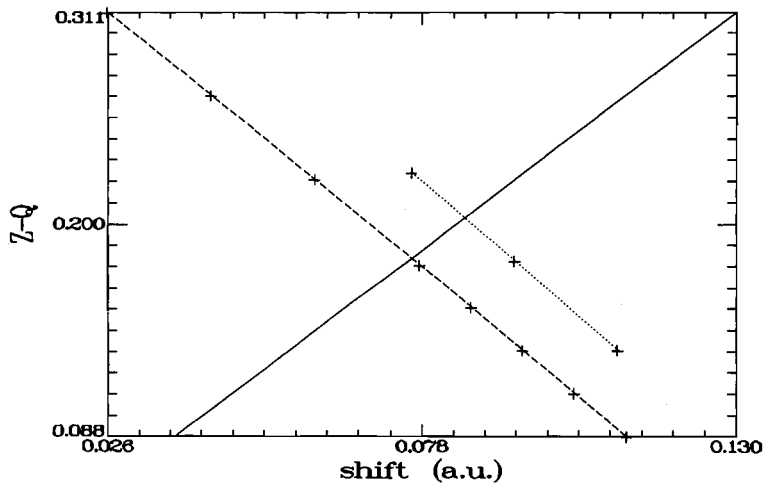


**Fig.1.** Results for the system Zn/Cu. Calculated charge transfer from (shown as positive) or towards (shown as negative) the impurity site obtained according to eqn.(2) of text (dashed line) as a function of the potential shift applied on the impurity potential. The variation given by eqn.1 is indicated by the solid line while the dotted line indicates the solution which includes corrections due to the redistribution of the impurity charge.



**Table 1.** Calculated total charge within impurity cell for Zn in Cu

| Ref.1a | Ref.2                                         | cc-CPA, Ref.2 | Ref.3  | Present work |
|--------|-----------------------------------------------|---------------|--------|--------------|
| 11.72  | 11.805 <sup>(1)</sup> (11.876) <sup>(2)</sup> | 11.801        | 11.795 | 11.818       |

<sup>(1)</sup> Result quoted in ref.2 referring to a single impurity calculation including the first shell of neighbours.

<sup>(2)</sup> Result by R.Zeller and co workers, quoted in ref.2, referring to a calculation in which all charges remain fixed except those of the impurity atom.

Similar calculations were carried out for the single impurity systems, niobium in Cu, vanadium in Cu, cobalt in Cu, titanium in Cu and nickel in Cu. In each of these systems the scattering parameters for the impurity atom (Nb, V, Co, Ti or Ni) were obtained from a self consistent calculation of pure Nb, pure V, pure Co, pure Ti or pure Ni respectively, each one of the impurities assumed on an fcc lattice with the pure Cu lattice constant. The intersection between the calculated variation of  $Q(\Delta)$  versus  $\Delta$  (for each impurity system) with the one describing the charge  $Q_i$  versus the shift  $\delta V_i$  according to eqn.(1) estimates the charge flow from or towards the impurity cell. The results are presented in Table 2 and are compared with those from Ref.1c. A similar approach was also found succesful for the case of a substitutional Cu impurity in a Ni host as shown in Table 2.

**Table 2.** Calculated total charge within impurity cell

| Impurity System | Nb/Cu | V/Cu | Ni/Cu | Co/Cu | Ti/Cu | Cu/Ni |
|-----------------|-------|------|-------|-------|-------|-------|
| Present work    | 3.68  | 4.32 | 9.84  | 8.90  | 3.07  | 11.00 |
| Ref.1c          | 3.79  | 4.33 | 9.98  | 8.89  | 3.21  |       |
| Ref.9           |       |      |       |       |       | 11.02 |

The above examples were chosen because they represent various states of charge transfer including cases like those of Zn/Cu and Ni/Cu for which the charge transfer is small and cases like Nb/Cu and V/Cu for which the charge transfer is quite large. There have also been a number of other calculations on these systems that we can compare with, including the calculation using the Johnson-Pinski method of Zn in Cu quoted in ref. 2. It can be seen from Tables 1 and 2 that the results of our calculations agree rather well with those obtained by the much more elaborate first-principles methods.

The deviations of our results from those obtained by more accurate calculations may be attributed partly to the redistribution of the electron charge within the impurity cell upon embedding the impurity atom in the host system. This have been checked by repeating our calculations for the case of Zn in Cu allowing this time the system to undergo a charge redistribution within the impurity cell for each energy shift  $\Delta$ . The so obtained variation  $Q_{sc} = Q_{sc}(\Delta)$  is shown in Fig.1 by a dotted line; its intersection with the line described by eqn.(1) results to a charge trasfer of 0.203 electrons (lost by Zn to Cu) which is approximately 10 per cent greater than the value found without allowing any charge redistribution within the impurity cell. A similar calculation for the system Nb/Cu indicated a 10 per cent decrease in the value of the charge transfer as a result of the charge redistribution.

In conclusion, we see that our proposed calculational approach allows one to perform impurity calculations in an efficient computational way which leads to results that are within 10 per cent of those obtained by more elaborate calculations. In the case of small charge transfer this discrepancy may be eliminated by allowing charge redistribution within the impurity shell. On the other hand, in the case of large charge transfer (like in the system Nb/Cu )) we found that corrections involving more distant neighboring atoms may be necessary. There is no doubt that the proper way to treat impurities in metals is to consider the impurity and several nearest neighbor shells as an impurity cluster to be embedded in the host lattice. This is, of course, a formidable calculation, and the time required to perform it increases as the cube of the number of atoms in the cluster. There are times when great precision may not be required for a given application, and it is interesting to note that there seems to be a much easier calculation that will give surprisingly good predictions for the charge on the impurity site. The success of these calculations also serves to give some insight into the physics of the impurity problem.

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## FREE GREEN FUNCTION FOR OVERLAPPING SPHERES

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## INTRODUCTION

The interest of removing the geometrical restrictions imposed by the muffin-tin approximation has been outlined by several authors (Natoli et al., 1986; Butler and Nesbet, 1990; Gonis, 1992; Foulis et al., 1995). The non muffin-tin methods are based on the partitioning of space into non-overlapping cells, that introduces discontinuities of the potential at cell boundaries. The usual method for treating general potential is slowly convergent (Butler, 1996). In 1978, Sun and Su (Sun and Su, 1978) proposed a multiple scattering theory for overlapping potentials based on a new representation of the Green function. In this paper, we point out a mistake in their paper, which invalidates their conclusions. We straighten up some loose ends in their calculation of the Green function and we stretch some applications.

The first section is devoted to the derivation of the two-center expansion of the Green function in overlapping spheres. This expansion is a notoriously difficult problem (Sack, 1964) that was finally solved by Sun and Su. In the second section, we discuss the use of this overlapping Green function.

## TWO-CENTER EXPANSIONS OF THE GREEN FUNCTIONS

$G_0(\mathbf{r} - \mathbf{r}')$  is the solution of the equation  $(\nabla^2 + \kappa^2)G_0(\mathbf{r} - \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$ , and it may be expressed into the following form:

$$G_0(\mathbf{r} - \mathbf{r}') = \frac{1}{2\pi^3} \int d^3q \frac{\exp[i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')] }{\kappa^2 - q^2}. \quad (1)$$

Denoting  $\mathbf{r} - \mathbf{r}' = (\mathbf{r}_i - \mathbf{R}_i) - (\mathbf{r}_j - \mathbf{R}_j) = \mathbf{r}_i - \mathbf{r}_j + \mathbf{R}_{ij}$ , the exponential function in Eq.(1) is rewritten as  $\exp(i\mathbf{q} \cdot \mathbf{r}_i) \exp(i\mathbf{q} \cdot \mathbf{R}_{ij}) \exp(-i\mathbf{q} \cdot \mathbf{r}_j)$ . The Bauer identity is used for each exponential term (Abramowitz and Segun, 1964). According to Friedman and Russek (Friedman and Russek, 1954), the obtained series is uniformly convergent. Hence  $f$  and  $\Sigma$  can be interchanged. By so doing, we obtain the following expression for the Green function:

$$G_0(\mathbf{r}_i, \mathbf{r}_j, \mathbf{R}_{ij}) = 8 \sum_{L'L''L} C_{-L'L''L} i^{l+l''-l'} Y_L(\hat{\mathbf{r}}_i) Y_{L''}(\hat{\mathbf{R}}_{ij}) Y_{-L'}(\hat{\mathbf{r}}_j) I(\kappa), \quad (2)$$

where we have defined the compound index  $L = (l, m)$ , the spherical harmonics  $Y_L = Y_l^m$ ,  $Y_{-L} = (-1)^m Y_l^{-m}$  and the Gaunt coefficient:

$$\begin{aligned} C_{-L'L''L} &= \int Y_{-L'}(\hat{\mathbf{q}}) Y_{L''}(\hat{\mathbf{q}}) Y_L(\hat{\mathbf{q}}) d\Omega \\ &= (-1)^{m'} \sqrt{\frac{(2l+1)(2l'+1)(2l''+1)}{4\pi}} \begin{pmatrix} l & l' & l'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l' & l'' \\ m & -m' & m'' \end{pmatrix}. \end{aligned}$$

We have to calculate the integral  $I(\kappa)$  of Eq.(2) which depends on the spherical Bessel functions and is expressed as:

$$I(\kappa) = \lim_{M \rightarrow +\infty} I_\epsilon^M(\kappa) = \lim_{M \rightarrow +\infty} \lim_{\epsilon \rightarrow 0} \int_\epsilon^M q^2 dq \frac{j_l(qr_i) j_{l''}(qR_{ij}) j_{l'}(qr_j)}{\kappa^2 - q^2}. \quad (3)$$

Since  $j_l(-qr) = (-1)^l j_l(qr)$  and  $l + l' + l''$  is even (property of the Gaunt coefficients),  $I_\epsilon^M(\kappa)$  is rewritten as follows:

$$I_\epsilon^M(\kappa) = \frac{1}{2} \left[ \int_{-M}^{-\epsilon} + \int_{+\epsilon}^M \right] q^2 dq \frac{j_l(qr_i) j_{l''}(qR_{ij}) j_{l'}(qr_j)}{\kappa^2 - q^2}. \quad (4)$$

According to Cauchy's theorem,  $2I_\epsilon^M(\kappa)$  plus the integral over the large half-circle  $C_M$  plus the integral over the small half-circle  $C_\epsilon$  (see Figures 1a and 1b) is equal to the residue. Hence we have to calculate these two integrals on the one hand, and the residue on the other hand.

In Eq. (4), after using the relation  $j_l = \frac{1}{2}(h_l^+ + h_l^-)$ , we obtain eight different terms, which are products of three Hankel functions. Then the integral  $I_\epsilon^M(\kappa)$  is carried out by the residue theorem using either the contour of Fig. 1a or the one of Fig. 1b. The choice of the contour depends on the asymptotic behavior of the three Hankel functions, which depends on the treated region: the non-overlapping region defined by  $r_i + r_j \leq R_{ij}$  or the overlapping region defined by  $|r_i - r_j| \leq R_{ij} \leq r_i + r_j$ . For example, the term  $h_l^+(qr_i) h_{l''}^-(qR_{ij}) h_{l'}^+(qr_j)$  behaves as  $i^{-l-l'+l''-1} \exp[iq(r_i - R_{ij} + r_j)] / qr_i qR_{ij} qr_j$  as  $|q|$  tends to  $+\infty$  (Abramowitz and Segun, 1964). Since  $r_i - R_{ij} + r_j$  is negative in the non-overlapping region, we have to use the lower contour for the integration, and since  $r_i - R_{ij} + r_j$  is positive in the overlapping region, we have to use the upper one. For each region, four of the eight terms are integrated by using the upper contour and the four other terms are integrated by using the lower contour.

Now, since the case of the non-overlapping region is well known (Natoli et al., 1986), we consider the overlapping region characterized by  $|r_i - r_j| \leq R_{ij} \leq r_i + r_j$ . Let's carry out the integration on the upper contour. This is achieved in three steps: firstly, we have to examine the asymptotic behavior when  $M$  tends to  $+\infty$ , secondly when  $\epsilon$  tends to 0 and thirdly, we

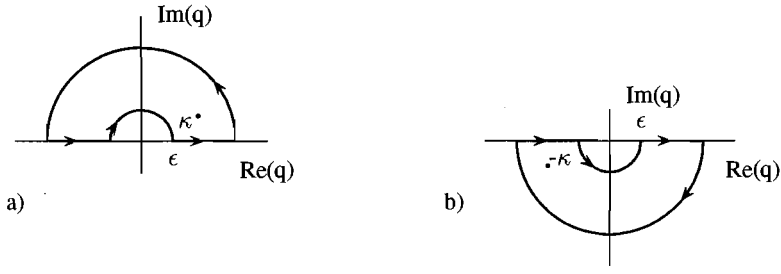


Figure 1: Contours used to calculate  $I(\kappa)$ : a) the upper contour, b) the lower contour.

have to calculate the residue.

- $M \rightarrow +\infty$

The integrand is expressed as:

$$S^+(q) = \frac{1}{8} \frac{q^2}{\kappa^2 - q^2} [h_l^+(qr_i)h_{l\nu}^+(qR_{ij})h_{l\nu}^+(qr_j) + h_l^+(qr_i)h_{l\nu}^+(qR_{ij})h_{l\nu}^-(qr_j) + h_l^+(qr_i)h_{l\nu}^-(qR_{ij})h_{l\nu}^+(qr_j) + h_l^-(qr_i)h_{l\nu}^+(qR_{ij})h_{l\nu}^+(qr_j)]. \quad (5)$$

Each Hankel function product tends exponentially fast to zero on the upper half-circle. Therefore the contribution of the integral over  $C_M$  tends to 0 when  $M \rightarrow +\infty$ .

- $\epsilon \rightarrow 0$

By using  $h_l^\pm = j_l \pm i n_l$ ,  $S^+(q)$  becomes:

$$S^+(q) = \frac{1}{8} \frac{q^2}{\kappa^2 - q^2} [4j_l(qr_i)j_{l\nu}(qR_{ij})j_{l\nu}(qr_j) + 2ij_l(qr_i)n_{l\nu}(qR_{ij})j_{l\nu}(qr_j) + 2ij_l(qr_i)j_{l\nu}(qR_{ij})n_{l\nu}(qr_j) + 2in_l(qr_i)j_{l\nu}(qR_{ij})j_{l\nu}(qr_j) + 2in_l(qr_i)n_{l\nu}(qR_{ij})n_{l\nu}(qr_j)]. \quad (6)$$

Now, we have to study the behavior of  $S^+(q)$  when  $\epsilon$  tends to 0. According to Abramowitz and Segun (Abramowitz and Segun, 1964),  $j_l(qr)$  behaves as  $\frac{(qr)^l}{(2l+1)!!}$  and  $n_l(qr)$  as  $\frac{-(2l-1)!!}{(qr)^{l+1}}$  when  $q$  tends to zero. The first four terms are regular at the origin and the integral over  $C_\epsilon$  tends to 0 when  $\epsilon \rightarrow 0$ . The last term, that is the product of three Neumann functions, is divergent at  $q = 0$ . For this term only, we have to calculate the contribution of the small half-circle. To do this, the following expansions are needed:

$$n_l(qr) = \frac{-(2l-1)!!}{(qr)^{l+1}} \sum_{s=0}^{+\infty} a_l^s \frac{(qr)^{2s}}{2^s} \text{ with } a_l^s = \frac{(2l+1)}{s! \prod_{i=0}^s (2l+1-2i)}, \quad (7)$$

$$\frac{1}{\kappa^2 - q^2} = \sum_{n=0}^{+\infty} \frac{q^{2n}}{\kappa^{2n+2}}, \text{ as } q \rightarrow 0. \quad (8)$$

The integral on the small half-circle  $C_\epsilon$  can be written as a sum of terms  $b_m \int_{C_\epsilon} q^{2m-1} dq$  with  $m = s + s' + s'' - \frac{1}{2}(l + l' + l'') + n$ . Thanks to the parity of  $l + l' + l''$ , this integral is equal

to  $-\pi a_m \delta_{m,0}$ . Since  $n \geq 0$ , only the terms corresponding to  $\frac{1}{2}(l + l' + l'') - (s + s' + s'') \geq 0$  are taken into account. Hence the integration on the small half-circle introduces the term:

$$\sum_{s+s'+s'' \leq \frac{1}{2}(l+l'+l'')} \rho_{ls}(\kappa r_i) \rho_{l''s''}(\kappa R_{ij}) \rho_{l's'}(\kappa r_j) \quad (9)$$

where

$$\rho_{ls}(\kappa r) = \frac{\sqrt{\pi}}{2} \frac{(-1)^{l+s} \left(\frac{\kappa r}{2}\right)^{2s-l-1}}{s! \Gamma\left(\frac{1}{2} - l + s\right)}. \quad (10)$$

### • Residue

Since  $\frac{q^2}{\kappa^2 - q^2} = \frac{1}{2} \left( \frac{q}{\kappa - q} - \frac{q}{\kappa + q} \right)$ , the upper contour contains only the pole  $q = \kappa$ , where  $\kappa$  has a positive imaginary part (Newton, 1982). The residue of  $S^+(q)$  calculated at this point is:

$$\begin{aligned} Res(S^+, \kappa) = & -\frac{i\pi}{2} \kappa j_l(\kappa r_i) j_{l''}(\kappa R_{ij}) j_{l'}(\kappa r_j) + \frac{\pi}{4} \kappa j_l(\kappa r_i) n_{l''}(\kappa R_{ij}) j_{l'}(\kappa r_j) \\ & + \frac{\pi}{4} \kappa j_l(\kappa r_i) j_{l''}(\kappa R_{ij}) n_{l'}(\kappa r_j) + \frac{\pi}{4} \kappa n_l(\kappa r_i) j_{l''}(\kappa R_{ij}) j_{l'}(\kappa r_j) \\ & + \frac{\pi}{4} \kappa n_l(\kappa r_i) n_{l''}(\kappa R_{ij}) n_{l'}(\kappa r_j). \end{aligned} \quad (11)$$

We follow the same reasoning for the integration on the lower contour, and adding the two contributions, we obtain the following expression for the Green function in the overlapping region:

$$\begin{aligned} G_0(\mathbf{r}_i, \mathbf{r}_j) = & \kappa \sum_{LL'} [ j_L(\kappa \mathbf{r}_i) J_{LL'}^{ij} j_{-L'}(\kappa \mathbf{r}_j) + \frac{i}{2} j_L(\kappa \mathbf{r}_i) J_{LL'}^{ij} n_{-L'}(\kappa \mathbf{r}_j) \\ & + \frac{i}{2} n_L(\kappa \mathbf{r}_i) J_{LL'}^{ij} j_{-L'}(\kappa \mathbf{r}_j) + \frac{i}{2} j_L(\kappa \mathbf{r}_i) N_{LL'}^{ij} j_{-L'}(\kappa \mathbf{r}_j) \\ & + \frac{i}{2} n_L(\kappa \mathbf{r}_i) N_{LL'}^{ij} n_{-L'}(\kappa \mathbf{r}_j) \\ & + \frac{i}{2} \sum_{ss'} \rho_{Ls}(\kappa \mathbf{r}_i) P_{LsL's'}^{ij} \rho_{-L's'}(\kappa \mathbf{r}_j) ] \end{aligned} \quad (12)$$

In Eq.(12),  $z_L(k\mathbf{r}_i) = z_l(kr_i) Y_L(\hat{\mathbf{r}}_i)$ ,  $z_{-L'}(k\mathbf{r}_j) = z_{l'}(kr_j) Y_{-L'}(\hat{\mathbf{r}}_j)$ , where  $z_l$  indicates  $j_l$ ,  $n_l$  or  $\rho_{ls}$ , and the propagators  $J_{LL'}^{ij}$ ,  $N_{LL'}^{ij}$  and  $P_{LsL's'}^{ij}$  are defined by:

$$J_{LL'}^{ij} = -4i\pi \sum_{L''} C_{-L'L''L} i^{l+l''-l'} j_{l''}(kR_{ij}) Y_{l''}(\hat{\mathbf{R}}_{ij}), \quad (13)$$

$$N_{LL'}^{ij} = -4i\pi \sum_{L''} C_{-L'L''L} i^{l+l''-l'} n_{l''}(kR_{ij}) Y_{l''}(\hat{\mathbf{R}}_{ij}), \quad (14)$$

$$P_{LsL's'}^{ij} = -4i\pi \sum_{\substack{L''s'' \\ s+s'+s'' \leq \frac{1}{2}(l+l'+l'')}} C_{-L'L''L} i^{l+l''-l'} \rho_{l''s''}(kR_{ij}) Y_{l''}(\hat{\mathbf{R}}_{ij}), \quad (15)$$

## DISCUSSION

The convergence properties of Eq. (12) was not investigated. Except for the first term, all terms of Eq. (12) are divergent when considered independently. This divergence can be cured

by a Borel summation, as in Zeller, 1987. It would be interesting to compare the numerical convergence of the Borel summation of Eq. (12) and of the standard expression of Zeller. However, it is still possible that the sum of the terms in Eq. (12) is convergent. Schadler (1992) performed a numerical test for the resolution of the Poisson's equation by using, in the overlapping region, the Green function worked out by Sack (Sack, 1964), which is the  $\kappa = 0$  limit of Eq. (12). He showed that the corrections due to the overlap are important and have to be taken into account and he obtained convergence for relative small  $l_{max}$  as compared to the calculation by Gonis et al. (Gonis et al., 1991). The last term of Eq. (12) compensates for the divergence of the next to the last term when  $\kappa \rightarrow 0$ . Moreover  $\Delta - \kappa^2$  operating on all terms gives zero, except for the last term which gives  $\delta(\mathbf{r} - \mathbf{r}')$  (in the case of non-overlapping spheres, this last term has no equivalent because  $\mathbf{r} = \mathbf{r}'$  is not possible and  $(\Delta - \kappa^2)G_0 = 0$ ). Similarly the expression given by Sack (Sack, 1964) is indeed a solution of  $\Delta G = \delta(\mathbf{r} - \mathbf{r}')$ . This contradicts the remark of Zhang et al. (Zhang et al., 1994).

Sun and Su (1978) have tried to derive the multiple scattering equations considering a "muffin-tin" potential with overlapping spheres. In their method, the molecular potential in the atomic overlapping spheres is defined as follows:  $V(\mathbf{r}) = \sum_i V^i(\mathbf{r}_i)$  with  $V^i(\mathbf{r}_i) = V_i(r_i)$  inside the atomic sphere  $i$  and 0 outside. They assume that the solution of the Lippmann-Schwinger equation in the whole sphere  $i$  (Eq. 35 of their paper) is equal to  $\Psi(\mathbf{r}_i + \mathbf{R}_i) = \sum_L C_L^i R_L^i(r_i) Y_L(\hat{\mathbf{r}}_i)$  while  $R_L^i(r_i)$  is the regular solution of the radial Schrödinger equation with the potential  $V^i(r_i)$ . Their method failed for two reasons. Firstly, in overlapping regions, if the potentials are overlapping, the solution of the Lippmann-Schwinger equation for the potential  $V_1 + V_2$  cannot be expressed from the solutions for  $V_1$  or  $V_2$ . Secondly, even in the case of non-overlapping potentials, linear combinations of regular or irregular solutions at the origin have to be used, as for the Green function. These points have not been noticed in the papers quoting Sun and Su (see, e.g., Keister, 1983). For the multiple scattering theory with general potentials, one can cut the potential into non-overlapping cells inscribed into overlapping spheres. Within each sphere, the wavefunction can be written as  $\sum A_L R_{iL}(\mathbf{r})$  for  $\mathbf{r}$  outside the neighboring spheres and  $\sum_L B_L R_{iL}(\mathbf{r}) + C_L S_{iL}(\mathbf{r})$  in the overlapping region, where  $R_{iL}$  is regular and  $S_{iL}$  is irregular at the origin. These new multiple scattering equations will be treated in a forthcoming publication.

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