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als—including iron oxides such as ferrihy-drite—often depend on the size of the nanoparticles. Elucidation of these size-dependent effects is crucial for understanding the roles of iron oxides in environmental and geologic processes, such as the biogeochemical cycling of iron, weathering, and respiration of iron by microorganisms. Nanocrystalline materials can be characterized by many techniques, including electron microscopy (see the figure, left panel). However, none of these methods have been adequate for the structural determination of materials that are commonly referred to as "x-ray amorphous" (11)—meaning that the diffraction peaks are so broad as to make it nearly or totally impossible to solve their structure with laboratory-based x-ray diffraction instrumentation.

Michel et al. have now performed total elastic scattering experiments on ferrihydrite, which is x-ray amorphous, and have analyzed the data with the atomic pair distribution function (PDF) method. To obtain their structure, the authors calculated the PDF using structural models and then compared it to the PDF obtained from the experimental data. In addition to proposing a new model for the structure of ferrihydrite (see the figure, middle and right panels), the authors show that other recent structural models for ferrihydrite, including one that has gained a reasonable level of "acceptance" (12), produce a worse fit with the experimental data. This makes their proposed structure all the more convincing.

PDF analysis enables the extraction of structural information from powder diffraction data. This approach has for some time been the tool of choice for studying the atomic structure of liquids and glasses. The availability of focused, high-energy x-ray beams and of fast area detectors and advanced data treatment strategies has made it possible to apply this method to poorly crystalline and nanocrystalline materials. For example, Petkov et al. have used the approach to examine the atomic structures of vanadia xerogel (13) and of gold nanoparticles in water (14).

In a PDF analysis, the PDF is obtained by Fourier transformation of the total elastic scattering data. Use of a high-energy x-ray beam, available at third-generation synchrotron x-ray sources, is crucial, because the short wavelengths enable collection of diffraction data at much higher resolution than can be achieved in the laboratory.

The resulting PDF is a real-space representation of interatomic distances that includes both the short-range (1 to 5 Å) and intermediate- to long-range correlations (5 to potentially more than 100 Å) for all pairs of atoms in the structure. The sensitivity, resolution, and extended range of information allow real-space fitting of structural models for nanocrystalline and disordered materials, without the detrimental peak-broadening effects incurred during structure refinement in reciprocal space.

As the study by Michel et al. shows, the PDF method is a powerful tool for elucidating the structures of natural and synthetic nanoparticulate materials. It can also be used to study how atomic structure varies as a function of particle size and environment, a matter of crucial importance both for designing new nanomaterials and for understanding the properties of natural materials such as ferrihydrite.

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PHYSICS

Is There Glue in Cuprate Superconductors?

Philip W. Anderson

Many theories about electron pairing in cuprate superconductors may be on the wrong track.

More than 20 years after the discovery of cuprate superconductors, physicists do not agree on what mechanism causes the loss of electrical resistance at temperatures as high as 160 K (known as T_c, the transition temperature). They do agree that electron pairs are crucial because they can form a condensate that flows without resistance, but the interaction that causes the pairs to form is disputed.

For many years, papers have been appearing that discuss the high-T_c copper oxide superconductors in the same terms as the conventional metallic superconductors (such as mercury or lead). That is, some researchers assume that the high-T_c materials involve electron pairs bound together by the exchange of bosons (a fundamental class of particles, the other being fermions). In the ordinary superconducting metals, these exchanged particles are phonons (atomic lattice vibrations)

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that act like a bosonic "glue" to hold the electron pairs together. Many alternatives have been proposed for this bosonic glue (1–9). This mythology is popular among science journalists, who dramatize both the element of competition and the search for The Secret.

I argue here that this need for a bosonic glue is folklore rather than the result of scientific logic. It comes from the inappropriate assumption that superconductivity in these materials is described by a mathematical framework called the Eliashberg formalism (10), which is an extension of the original ideas of Bardeen, Cooper, and Schrieffer. In the 1960s, Morel and I (11) and Schrieffer et al. (12) adapted this formalism to calculate properties of the conventional superconductors, but it is valid only to describe the particular mechanism that explains these superconductors.

Electrons only interact, to a very good approximation, via the Coulomb interaction. This is the elementary electrical force that causes two negative charges to repel each other. So how can this repulsion between electrons be eliminated in favor of electron pair

binding? The possibilities are either "dynamic screening" or a mechanism suggested by Pitaevskii (13) and by Brueckner et al. (14) of putting the electron pairs in an anisotropic wave function (such as a d-wave), which vanishes at the repulsive core of the Coulomb interaction. In either case, the paired electrons are seldom or never in the same place at the same time. Dynamic screening is found in conventional superconductors, and the anisotropic wave functions are found in the high-T_c cuprates and many other unconventional superconductors.

In the case of dynamic screening, the Coulomb interaction e^2/r (where e is the electron charge and r is the distance between charges) is suppressed by the dielectric constant of other electrons and ions. The plasma of other electrons damps away the long-range $1/r$ behavior and leaves a screened core, $e^2 \exp(-\kappa r)/r$ (where κ is the screening constant), that acts instantaneously, for practical purposes, and is still very repulsive. By taking the Fourier transform of the interaction in both space and time, we obtain a potential energy V, which is a function of frequency ω and wavenumber q; the screened Coulombic core, for instance, transforms to $V_s = e^2/(q^2 + \kappa^2)$ and is independent of frequency. This interaction must then be screened by the dielectric constant ε_{ph} because of polarization of the phonons, leading to a final expression $V = e^2/[(q^2 + \kappa^2)\varepsilon_{ph}(q, \omega)]$. This dielectric constant is different from 1 only near the lower frequencies of the phonons. It screens out much of the Coulomb repulsion, but "overscreening" doesn't happen: When we get to the very low frequency of the energy gap, V is still repulsive.

Instead of accounting for the interaction as a whole, the Eliashberg picture treats only the phonon contribution formally, replacing the high-frequency part of the potential with a single parameter. But the dielectric description more completely clarifies the physics, and in particular it brings out the limitations on the magnitude of the interaction. That is, it makes clear that the attractive phonon interaction, characterized by a dimensionless parameter λ, may never be much bigger, and is normally smaller, than the screened Coulomb repulsion, characterized by a parameter μ (11). The net interaction is thus repulsive even in the phonon case.

How then do we ever get bound pairs, if the interaction is never attractive? This occurs because of the difference in frequency scales

of the two pieces of the interaction. The two electrons about to form a pair can avoid each other (and thus weaken the repulsion) by modifying the high-energy parts of their relative wave function; thus, at the low energies of phonons, the effective repulsive potential becomes weaker. In language that became familiar in the days of quantum electrodynamics, we can say that the repulsive parameter μ can be renormalized to an effective potential or "pseudopotential" μ^*. The effective interaction is then $-(\lambda - \mu^*)$, which is less than zero, hence attractive and pair-forming. One could say that superconductivity results from the bosonic interaction via phonons; but it is equally valid to say instead that it results from the renormalization that gives us the pseudopotential μ^* rather than μ. This does not appear in an Eliashberg analysis; it is just
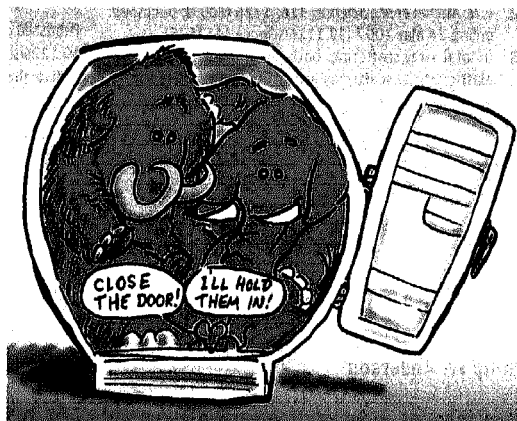
"We have a mammoth and an elephant in our refrigerator—do we care much if there is also a mouse?"

the type of correction ignored in this analysis.

The above is an instructive example to show that the Eliashberg theory is by no means a formalism that universally demonstrates the nature of the pairing interaction; it is merely a convenient effective theory of any portion of the interaction that comes from low-frequency bosons. There is no reason to believe that this framework is appropriate to describe a system where the pairing depends on entirely different physics.

Such a system occurs in the cuprate superconductors. The key difference from the classic superconductors, which are polyelectronic metals, is that the relevant electrons are in a single antibonding band that may be built up from linear sums of local functions of x^2-y^2 symmetry, with a band energy that is bounded at both high and low energies. In such a band the ladder-sum renormalization of the local Coulomb repulsion, leading to the pseudopotential μ^*, simply does not work, because the interaction is bigger than the energy width of

the band. This is why the Hubbard repulsion U between two electrons on the same atom (which is the number we use in this case to characterize the repulsion) is all-important in this band. This fact is confirmed by the Mott insulator character of the undoped cuprate, which is an antiferromagnetic insulator with a gap of 2 eV, giving us a lower limit for U.

But effects of U are not at all confined to the cuprates with small doping. In low-energy wave functions of the doped system, the electrons simply avoid being on the same site. As a consequence, the electrons scatter each other very strongly (15) and most of the broad structure in the electrons' energy distribution functions (as measured by angle-resolved photoelectron spectroscopy) is caused by U. This structure may naïvely be described by coupling to a broad spectrum of bosonic modes (4), but they don't help with pair binding. U is a simple particle-particle interaction with no low-frequency dynamics.

A second consequence of U is the appearance of a large antiferromagnetic exchange coupling J, which attracts electrons of opposite spins to be on neighboring sites. This is the result of states of very high energy, and the corresponding interaction has only high-frequency dynamics, so it is unrelated to a "glue." There is a common misapprehension that it has some relation to low-frequency spin fluctuations (16, 17), but that is incorrect, as low-frequency spin interactions between band electrons are rigorously ferromagnetic in sign. One can hardly deny the presence of J given that it has so many experimental consequences.

In order to avoid the repulsive potential these systems are described by the alternative Pitaevskii-Brueckner-Anderson scheme with pairing orthogonal to the local potential. Two such pairings exist, d-wave and "extended s-wave," but only one appears as a superconducting gap; the extended s-wave is unsuitable for a gap and acts as a conventional self-energy (18). The specific feature of the low-dimensional square copper lattice that is uniquely favorable to high T_c is the existence of the two independent channels for pairing (18). Because of the large magnitude of J, the pairing can be very strong, but only a fraction of this pairing energy shows up as a superconducting T_c, for various rather complicated but well-understood reasons.

The crucial point is that there are two very strong interactions, U (>2 eV) and J (~0.12 eV), that we know are present in the cuprates, both a priori and because of incontrovertible experimental evidence. Neither is properly described by a bosonic glue, and between the two it is easy to account for the

existence of antiferromagnetism, d-wave superconductivity, and many other phenomena of high-T_c superconductivity. Whether any additional "glue" exists is of lesser interest. We have a mammoth and an elephant in our refrigerator—do we care much if there is also a mouse?

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CHEMISTRY

Making Energy Count

F. Fleming Crim

Experiments reveal the subtle roles of vibrational and translational energy in reactions of polyatomic molecules.

Energy influences the rates of chemical reactions dramatically (1). Simply heating a reaction mixture deposits energy indiscriminately in internal and translational motion, but more specific excitation can change the course of a reaction. The challenge is to distinguish the effect of these different types of energy.

For reaction of atoms with diatomic molecules, knowledge of the geometry of the system at the energy barrier for the reaction is sufficient to predict the relative efficacy of vibrational and translational energy (2). However, few experimental studies have investigated the effectiveness of different types of energy in more complicated molecules. On page 1723 of this issue, Yan et al. (3) explore the role of vibrational and translational energy in a prototypical reaction of a polyatomic molecule.

Chemical kinetics centers on the concepts of a transition state (the geometry through which reactants pass as they rearrange their bonds to become products) and of a reaction coordinate (the minimum-energy path along which the atoms move to reach and pass through the transition state). To react, molecules must have sufficient energy to reach the transition state, and this energy must reside in motions that carry the system through the transition state.

Two-dimensional energy plots along the reaction coordinate for the reaction of A with BC (see the figure, top panel) convey little information about the motions involved. Varying the angle between A and BC pro-

duces a family of three-dimensional surfaces, one for each angle, that form a four-dimensional hypersurface. The best we can do in three dimensions is a "cut" through this hypersurface for a single angle (see the figure, bottom panel).

The situation is more complex for poly-

atomic molecules. The reaction hypersurface has more dimensions, and there are often several transition states leading to different products. Perhaps most important, there are many more vibrations in the reactant. Nevertheless, the concepts of a reaction coordinate and transition state remain useful for understanding the role of different types of energy in these reactions.

Yan et al. study the reaction of Cl with CHD_3, which has two available paths: One breaks the C-H bond to form $HCl + CD_3$, and the other breaks the C-D bond to form $DCl + CHD_2$. Stretching of the reactant bond appears to be part of the motion along the reaction coordinate. Therefore, an intuitively appealing means of accelerating a reaction is to place vibrational energy in the bond that is to be broken. This approach is a proven means of preferentially cleaving the vibrationally excited bond in the reactions of Cl with partially deuterated methanes (4, 5). These experiments also show that vibrational excitation

Reaction dynamics. In the reaction studied by Yan et al., the CD_3 group is the "atom" C, and Cl and H are the atoms A and B, respectively. **(Top)** Two-dimensional view of the energy along the reaction coordinate for the reaction A + BC→AB + C. The highest energy point is the transition state. **(Bottom)** Three-dimensional view of the energy surface for the reaction shown at the top, along with a contour plot of the surface. The geometry of A-B-C is linear. The coordinates are the length of the "new" bond, R_{AB}, and the length of the "old" bond, R_{BC}. The red line is the reaction coordinate.
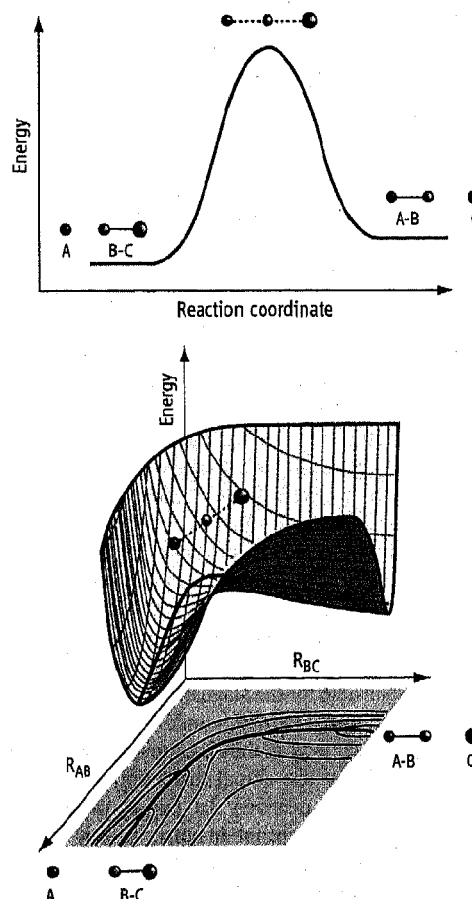
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