Z. Phys. D 40, 262–264 (1997)

ZEITSCHRIFT
FÜR PHYSIK D

Optical response of Ag clusters

Llorenç Serra[1], **Angel Rubio**[2]

[1] Departament de Física, Universitat de les Illes Balears, E-07071 Palma de Mallorca, Spain
[2] Departamento de Física Teórica, Universidad de Valladolid, E-47011 Valladolid, Spain

Received: 4 July 1996

Abstract. The dielectric model proposed by Liebsch is solved for Ag clusters within time dependent density functional theory. The distribution of oscillator strength is analyzed and departures from the behaviour of simple (alkali) clusters are stressed. Comparison with experimental results of isolated Ag_N^+ clusters is made. The observed blueshift as the size of the cluster decreases is explained by a reduction of the s-d screening interaction in the surface region. As a microscopic justification of the model, the response of the Ag^+ core is calculated using the embedded atom approximation.

PACS: 36.40.+d; 31.50.+w

Metallic clusters of Ag atoms have recently drawn much interest because of the new features observed in their collective properties. As in alkali clusters, their optical response is characterized by the presence of resonant surface plasmon states related to the collective motion of delocalized electrons. However, an important difference stems from the fact that the core d electrons of silver form as a function of size a polarizable background that strongly screens the interaction between valence electrons. This modified interaction is responsible for the deviation of the finite cluster, planar-surface and bulk response from the behaviour of simple (alkali) metals. In clusters the most clear manifestation of this deviation from simple behaviour [1] is the blueshift of surface plasmon energy with decreasing cluster size observed in isolated Ag_N^+ clusters [2].

The situation is similar to that found for Ag surfaces. In the context of surfaces, Liebsch has proposed a model [3] which includes effects associated to the polarization of the $4d$ core electrons by means of an effective dielectric function $\epsilon_d(\omega)$ of the corresponding bulk metal. This dielectric function is used in the Poisson equation to obtain the induced Coulomb potential for valence electrons, and takes into account the modified interaction between valence electrons in the presence of the polarizable background. The model also considers the fact that the metallic layer close to the surface is actually less polarizable than the inner part and, therefore, the extension of the dielectric volume ends at a distance d from the surface. The dielectric function $\epsilon_d(\omega)$ is known from experiment [4] and constitutes an input of the model.

Using the result obtained with the dielectric model for the infinite surface, the response function for spherical particles in the limit of large particle radius has been explored in [2, 3]. With the same dielectric model, the cluster response has also been investigated by Kresin [5] using the Thomas-Fermi method to describe the interaction between valence electrons. By considering a polarization-free surface layer Kresin has shown that the unusual blueshift with decreasing size can be qualitatively explained by the Thomas-Fermi solution. This had also been shown by Lipparini and Pederiva [6] using sum-rule techniques in a similar model. In particular, the competition between core polarization and electronic spill-out was estimated analytically in [6].

Our aim in this paper is to analyze the cluster response with the dielectric model by using the time dependent local-density-approximation (TDLDA) to describe the rest of valence electron interactions. In this way, the dielectric model is solved in the same spirit as was originally proposed in [3], and we can also provide additional support to the results of [2, 3, 5, 6]. Moreover, from the TDLDA cluster response function we find additional predictions of the dielectric model, like the detailed distribution of oscillator strength, a sizeable modification of the integrated cross section or energy-weighted sum rule, and enhancement of the static polarizability. Finally, and in order to provide a microscopic justification of the model, we calculate the polarization of the Ag cores using the embedded atom approximation and compare with the result inferred from the Clausius-Mossotti relation using the experimental dielectric function $\epsilon_d(\omega)$.

To solve the TDLDA response equations [7] in the dielectric model we first obtain the modified Coulomb interaction between valence electrons. For this we use the result of [8], but now with the assumption of a dielectric $\epsilon_d(\omega)$ within a sphere of radius R_d, and $\epsilon = 1$ (vacuum) outside. R_d will be in general smaller than the jellium radius R, i.e., $R_d = R - d$. This describes a surface layer of thickness d which does not polarize in the cluster response and consequently is not contained in the dielectric effective volume. We note that the larger s-d screening is obtained when the induced charge density is localized in the polarizable medium.

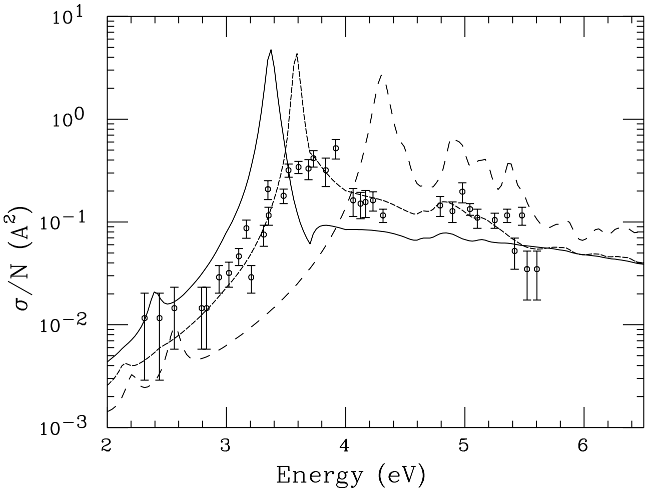

Fig. 1. Photoabsorption cross section per electron of Ag_{59}^+ in dipole approximation within the jellium model (*long dashed line*) and dielectric model with $d = 0$ (*solid*) and $d = 2a_0$ (*short dashed*). The experimental points are from [2] and for cluster $\mathrm{Ag}_{70\pm5}^+$. The experimental results of $\sigma(\omega)/N$ for $\mathrm{Ag}_{70\pm5}^+$ and $\mathrm{Ag}_{50\pm3}^+$ show only minor differences

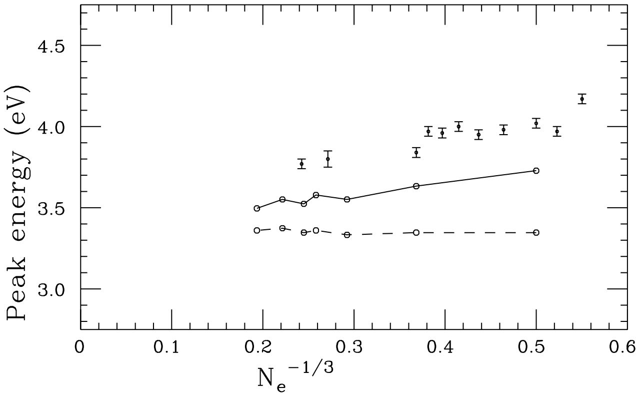

Fig. 2. Evolution of the plasmon peak energy with size in the dielectric model with $d = 0$ (*data points joined* with *dashed lines*) and with $d = 2a_0$ (*points joined* with *solid lines*). Experimental results are from [2]

Since the centroid of induced charge is close to the surface for the density oscillations associated to the surface plasmon it can be easily recognized that the surface layer will play an important role in determining the oscillation energy. This is also relevant when explaining the different behaviour observed for positive and negatively charged silver clusters [2].

Figure 1 shows the cross section of Ag_{59}^+ within the dielectric model with a surface layer thickness of $d = 0$ (solid line) and $d = 2a_0$ (short dashed line), in comparison with the result of the plain jellium model with $r_s = 3$ (long dashed line) and with the experimental data of [2]. It is evident from the figure the capability of the dielectric model to explain the experimental findings. The plasmon energy is shifted from the jellium value to smaller energies as a result of the dielectric polarization, that can be easily understood by noticing that the larger the screening the less energy is needed to create a collective mode. This shift is reduced when a surface layer without dielectric is considered and the induced charge density lies close to this surface. The result with $d = 2a_0$ has a plasmon energy in much better agreement with experiment. This proves that, indeed, the reduction of s-d screening at the surface layer is essential in order to explain the optical response of Ag_N^+ clusters. The value of $d = 2a_0$ is a little larger than the value proposed by Liebsch of $d = 1.5a_0$ for the planar surface showing that some finite size effects are also present in the model. This implies a reduction of the surface layer thickness as the size of the cluster increases, which is connected with the formation of the effective d-polarizable background. A more detailed study of these effects is lead for a forthcoming work [9].

Table 1. Integrated cross section in the range $[0, 10]$ eV divided by the sum-rule value (1) within the different models

N	Jellium	Dielectric	
		$d = 0$	$d = 2a_0$
20	0.99	0.85	0.87
40	0.98	0.83	0.85
58	0.99	0.82	0.78
92	0.96	0.80	0.76

Considering the distribution of oscillator strength, we notice that the jellium result greatly overestimates the strength on the high energy side of the plasmon peak (from approximately 4.5 to 5.5 eV). This is nicely corrected by the dielectric model and, in fact, the result with $d = 2a_0$ describes well this region. However, the plasmon peak at ≈ 3.6 eV is too narrow and also too high. The experiment indicates that some additional fragmentation of the plasmon peak, not accounted by our spherical model, is present.

An interesting prediction of the dielectric model is the sizeable modification of the integrated cross section. The integrated cross section model is provided by the energy weighted sum rule, which may be stated as

$$\int_0^\infty d\omega\, \sigma(\omega) = 4\pi^2\alpha\frac{\hbar^2}{2m}N\ , \tag{1}$$

where α is the fine structure constant and N the number of electrons. This result is the well known Thomas-Reiche-Kuhn sum rule and is valid for any interaction between electrons depending locally on their positions (as, e.g., the bare Coulomb $1/|\mathbf{r}_1 - \mathbf{r}_2|$). Within the dielectric model the electron-electron interaction is modified depending on the excitation energy ω [8] and this is ultimately reflected in the integrated oscillator strength. Due to this dependence of the effective interaction the analytical sum rule within the dielectric model is not as straightforward as (1) and is more easily analyzed by direct integration of the computed cross section. From Table 1 we see that the modification consists typically in a sizeable reduction of 15-20%. This is clearly showing that the mechanism of core polarization is transferring a sizeable amount of strength from valence to core response. Alternatively this fact may be interpreted as a reduction of the effective number of electrons participating in the cluster optical response.

Figure 2 shows the evolution of plasmon energy with size for Ag_N^+ clusters for $d = 0, 2a_0$. The experimental data are again the measurements of [2]. As was anticipated in [3, 5] the blueshift with decreasing size is explained within the dielectric model by the non polarizable surface layer. In the absence of this, the dependence with size is flat. Our

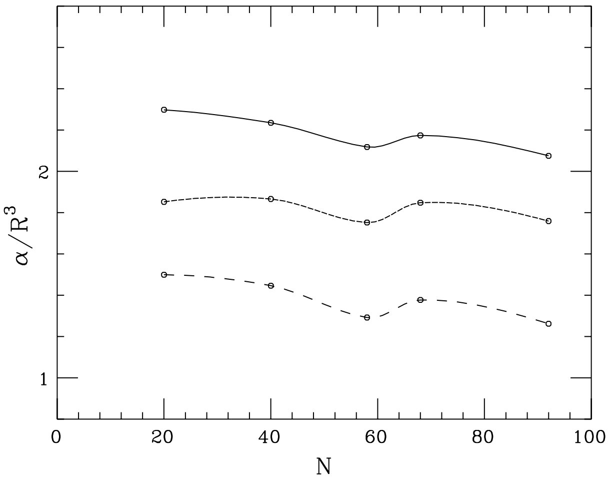

Fig. 3. Static dipole polarizability of neutral Ag$_N$ clusters in the jellium model (*long dashed lines*) and dielectric model with d = 0 (*solid*) and d = 2a_0 (*short dashed*)

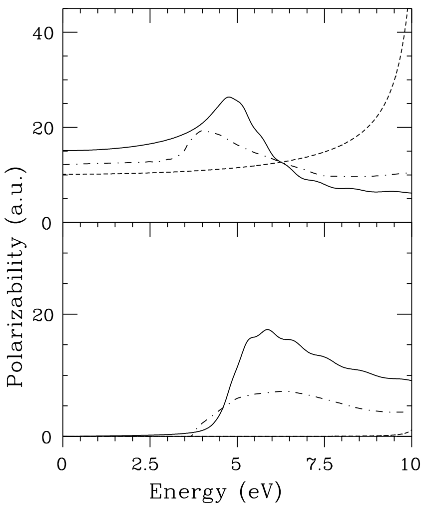

Fig. 4. *Upper* and *lower panels* show respectively the real and imaginary parts of the Ag$^+$ core polarizability. *Solid line* corresponds to the embedded core approximation while *short dashed* one to the free Ag$^+$ ion. *Dashed-dotted line* shows the result obtained from the experimental $\epsilon_d(\omega)$ [4] using the Clausius-Mossotti relation. See text

results indicate that a larger value of d would provide a better agreement with experiment.

In Fig. 3 we show the prediction of the dielectric model for the static polarizability of neutral Ag$_N$ clusters. These experimental measurements have been performed for the case of alkali clusters [10] and, when done for Ag, would provide valuable information against which the prediction of the dielectric model could be confronted. In particular, we find that the static polarizability is quite sensitive to the value of the surface layer thickness. Thus experimental polarizability data should be used to quantify the size-evolution of the surface thickness.

With the results presented, specially those of Figs. 1,2, we conclude that the dielectric model indeed explains the basic features of the optical response of Ag clusters. The role of the surface non-polarizable layer is very important for that purpose. In addition, we have emphasized that the model predicts a reduction of 15-20% of the number of electrons participating in the cluster response.

In order to provide a more microscopic justification of the dielectric model we have calculated the polarizability of an Ag$^+$ core embedded at the center of the jellium sphere of the cluster, and compare it in Fig. 4 with the result we obtain for the free Ag$^+$ ion and with the polarizability which can be inferred by using the experimental $\epsilon_d(\omega)$ in the Clausius-Mossotti relation

$$\alpha_c(\omega) = \frac{\epsilon_d(\omega) - 1}{\epsilon_d(\omega) + 2}\, r_s^3 \; . \tag{2}$$

It can be seen in Fig. 4 that the behaviour of the computed embedded core polarizability resembles that inferred from the Clausius-Mossotti relation, both having a peak in the real part around 5 eV, while the imaginary part appreciably grows from zero around 3.5 eV. The free ion polarizability has a slightly lower value of Re$\{\alpha\}$ at lower energies but for $\omega > 6$ eV is quite higher and displays a sharp peak beyond 10 eV. On the contrary, the imaginary part is almost zero in the range $[0, 10]$ eV. This different behaviour must be attributed to the fact that in the embedded Ag$^+$ core the core-valence transitions are suppressed by the Pauli principle and this does not allow the formation of a sharp peak which almost exhausts the sum rule as in the free Ag$^+$.

From Fig. 4 we can conclude that the microscopic polarizability of the embedded core is qualitatively similar to that which is inferred from the experimental $\epsilon_d(\omega)$. We will use this polarizability in a future work to formulate an ab-initio cluster response for valence electrons including core polarization without invoking any experimental $\epsilon_d(\omega)$ information and the associated Poisson equation [9].

This work was supported in part by DGICyT grants PB92-0021-C02-02 and PB92-0645, and JCL (Grant VA25/95). Financial support for travel from the Universitat de les Illes Balears is gratefully acknowledged.

References

1. Brack M.: Rev. Mod. Phys. **65**, 677 (1993)
2. Tiggesbäumker J., Köller L., Meiwes-Broer K. -H., Liebsch A.: Phys. Rev. A **48**, R1749 (1993)
3. Liebsch A.: Phys. Rev. Lett. **71**, 145 (1993); Phys. Rev. B **48**, 11317 (1993)
4. Ehrenreich H., Philipp H. R.: Phys. Rev. **128**, 1622 (1962)
5. Kresin V. V.: Phys. Rev. B **51**, 1844 (1995)
6. Lipparini E., Pederiva F.: Z. Phys. D **27**, 281 (1993)
7. Ekardt W.: Phys. Rev. Lett. **52**, 1925 (1984); Phys. Rev. B **29**, 1558 (1984)
8. Rubio A., Serra Ll.: Phys. Rev. B **48**, 18222 (1993); Z. Phys. D **26**, 5118 (1993)
9. Serra Ll., Rubio A.: (work in progress); Phys. Rev. Lett. **78**, 1428 (1997) (Added in proof)
10. Knight W. D., Clemenger K., de Heer W. A., Saunders W. A., Phys. Rev. B **31**, 2539 (1985)