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Far-infrared absorption in small metallic particles

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The infrared-absorption properties of various configurations of small metallic particles, both aggregated and isolated, are analyzed. The effects of the amorphous oxide layers covering the particles are included. The dependence of the absorption on cluster shape is investigated, and the results obtained from two theoretical models for the dielectric constant of the aggregates are compared.

I. INTRODUCTION

Tanner *et al.*[1] and Granqvist *et al.*[2] have recently performed infrared-absorption measurements on small metal particles. The measured absorption was a few orders of magnitude stronger than that calculated from either the Gorkov and Eliashberg theory[3] or the classical Drude theory. Simanek[4] has suggested that the effect was mainly due to the amorphous oxide which surrounded the metallic particles. In his calculations it was assumed that the particles formed elongated cylindrical clusters. In order to assess the model proposed by Simanek, we have performed detailed calculations of the optical properties of various metal-oxide configurations. These will also provide some indications about possible modifications and improvements of the model. We first discuss the various models of isolated and aggregated particles and then present the results of numerical calculations for the case of Al particles. Qualitatively similar results are expected for other metals.

II. ISOLATED SPHERES

A. Metal spheres

The average dielectric constant as given by the Maxwell-Garnett (MG) theory[5,6] is

$$\epsilon_{\text{av}}=[\epsilon(1+2f)+2(1-f]/[\epsilon(1-f)+2+f]. \tag{1}$$

Here f is the volume fraction occupied by the spheres (the rest being vacuum), and ϵ is the dielectric constant of the metal, for which we employ the Drude formula

$$\epsilon=1-\omega_p^2/\omega(\omega+i\omega_c), \tag{2}$$

where ω_p is the plasma frequency and ω_c is the electron-collision frequency. Due to collisions of the electrons with the particle surfaces, ω_c deviates from its value ω_0 in bulk crystals and is given by[7]

$$\omega_c=\omega_0+v_F/r_1, \tag{3}$$

where r_1 is the sphere radius and v_F is the Fermi velocity.

The absorption coefficient of the medium is

$$\alpha=(\omega/c)\,\text{Im}(\epsilon_{\text{av}})/n_{\text{av}}, \tag{4}$$

where $n_{\text{av}}=\text{Re}(\epsilon_{\text{av}}^{1/2})$ is the refractive index.

The MG theory does not account for absorption due to eddy-current losses, which becomes appreciable for metal particles larger than about 50 Å in diameter. This magnetic absorption contributes an additional term α_m to the absorption coefficient[1]

$$\alpha_m=(f/10r_1)[(\omega/c)r_1]^3\,\text{Im}(\epsilon). \tag{5}$$

B. Oxide-coated metal spheres

The generalization of the MG theory to this case has been given by Weaver *et al.*[8] The absorption coefficient is again given by Eq. (4) with the following average dielectric constant:

$$\epsilon_{\text{av}}=\frac{f(r_1/r_2)^3\epsilon A+f[1-(r_1/r_2)^3]\epsilon_s B+1-f}{f(r_1/r_2)^3A+f[1-(r_1/r_2)^3]B+1-f}, \tag{6}$$

$$A=\frac{9\epsilon_s}{(\epsilon_s+2)(\epsilon+2\epsilon_s)-2(\epsilon_s-1)(\epsilon_s-\epsilon)(r_1/r_2)^3}, \tag{7}$$

$$B=\frac{3(\epsilon+2\epsilon_s)}{(\epsilon_s+2)(\epsilon+2\epsilon_s)-2(\epsilon_s-1)(\epsilon_s-\epsilon)(r_1/r_2)^3}. \tag{8}$$

Here ϵ_s is the dielectric constant of the oxide shell, r_1 and r_2 are its inner and outer radii, respectively, and f is the volume fraction occupied by the oxidized spheres (metal cores plus oxide shells). For the dielectric constant of the amorphous Al_2O_3 shell we employ the approximate expression suggested by Simanek[4]

$$\epsilon_s=10+ia\omega, \tag{9}$$

with $a=2\times10^{-14}$ sec.

In order to account for magnetic absorption a term of the form (5) is again added, but with f replaced by $f(r_1/r_2)^3$, since eddy-current losses occur in the metallic cores only.

In the limit of small f the absorption calculated from the equations given above should coincide with that obtained from the Mie theory. Since our calculations are restricted to f values not larger than 0.04, we have employed both methods and indeed found that they yield practically the same results. This also served to confirm the validity of the coated-sphere version of the MG theory, Eqs. (6)–(8), which has not been ascertained before. The relevant formulas of the Mie theory for both bare and coated spheres can be found in, e.g., Kerker's book.[9]

III. AGGREGATED SPHERES

In Simanek's model the spheres aggregate to form long cylinders. Each cylinder contains spherical metallic particles embedded in an amorphous oxide matrix. In order to investigate the role played by the shape of the aggregates, we treat a more general case and assume that the clusters have the shape of prolate spheroids. By varying the minor-to-major axis ratio b/a we can then cover cluster shapes ranging from spherical ($b/a=1$) to cylindrical ($b/a=0$).

Let ϕ be the volume fraction of the metallic spheres in the spheroid. Assuming that each sphere contributes its oxide layer to the formation of the spheroidal aggregate we have $\phi=(r_1/r_2)^3$. The dielectric constant of each aggregate, as given by the MG theory, is

$$\epsilon_a=\epsilon_s\frac{\epsilon(1+2\phi)+2\epsilon_s(1-\phi)}{\epsilon(1-\phi)+\epsilon_s(2+\phi)}\,. \tag{10}$$

The absorption coefficient of randomly oriented spheroids, of volume density f, is given by[10]

$$\alpha=f(\omega/c)\,\mathrm{Im}(a_1+a_2+a_3)\,, \tag{11}$$

where

$$a_i=\frac{4\pi}{3N_i}\,\frac{\epsilon_a-1}{\epsilon_a-1+(4\pi/N_i)}\,. \tag{12}$$

N_1 and $N_2=N_3$ are the depolarization factors of the prolate spheroid, which are given by

$$N_1=4\pi\frac{1-e^2}{e^2}\left(\frac{1}{2e}\ln\frac{1+e}{1-e}-1\right)\,, \tag{13}$$

$$N_1+2N_2=4\pi\,, \tag{14}$$

where $e=[1-(b/a)^2]^{1/2}$.

Since the metal filling fraction ϕ is not small, the validity of the MG formula (10) used by Simanek could be questioned.[11] Therefore, we also employ the alternative "effective-medium theory," according to which the dielectric constant ϵ_a of the aggregates is given by[11,12]

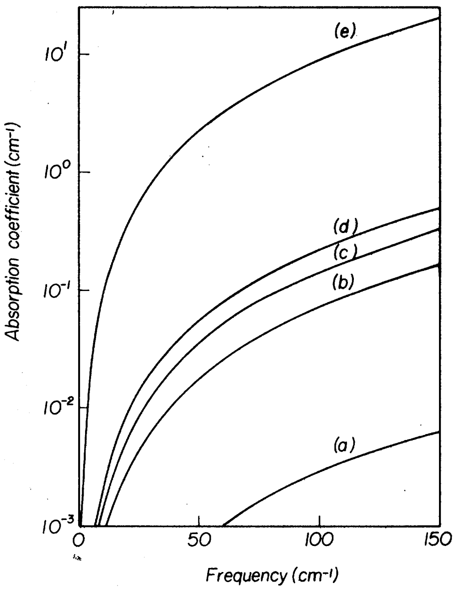

FIG. 1. Absorption coefficient of isolated spheres of diameter 50 Å and volume fraction 0.015: Unoxidized Al (a), and with oxide layers of thickness 5 Å (b), 10 Å (c), and 25 Å (fully oxidized) (d). Curve (e) represents the experimental results.

$$\frac{3\phi}{2+\epsilon/\epsilon_a}+\frac{3(1-\phi)}{2+\epsilon_s/\epsilon_a}=1\,. \tag{15}$$

IV. CALCULATIONS

For the numerical calculations we have chosen two sphere sizes for which experimental data are available. For the optical parameters appearing in Eq. (2) the experimental values of Al as given by Kloos[13] have been employed. The absorption coefficient of isolated spheres of diameter 50 Å and volume fraction $f=0.015$ is shown in Fig. 1. Curve a is for unoxidized spheres. Curves b, c, and d show how the absorption changes when an oxide layer develops and increases in thickness. In these calculations we have kept the outer radius fixed at 25 Å, so that an increase in the thickness of the oxide shell reduces the size of the metallic core. From these results it can be concluded that absorption in the oxide shells is the dominant loss mechanism (even for thin shells). However, for reasonable values of the oxide thickness, the calculated absorption is lower than the experimentally measured one,[2] curve e of Fig. 1, by about two orders of magnitude.

The effects of aggregation are demonstrated in Fig. 2, which shows the absorption by spheroidal clusters of various eccentricities. The labels on the calculated curves give the appropriate major-to-minor-axis ratios. The spheres which form the aggregates are again of diameter 50 Å, and for the oxide-shell thickness the experimental value of

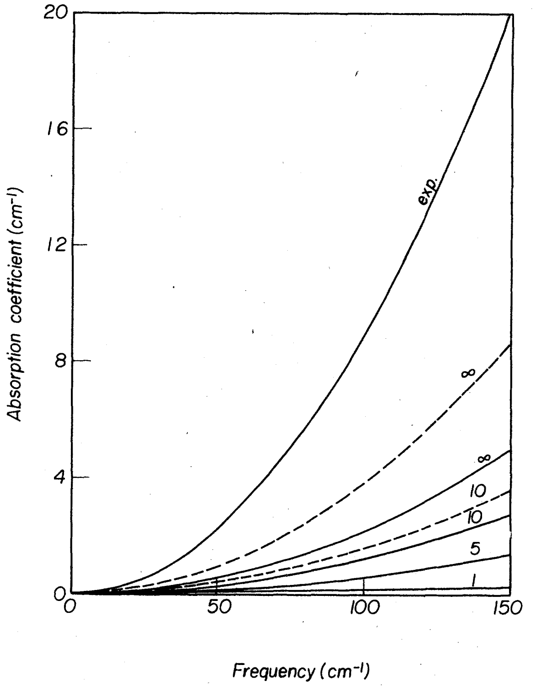

FIG. 2. Absorption coefficient of oxidized Al spheres of diameter 50 Å, with oxide layer thickness of 10 Å, aggregated into prolate-spheroidal clusters, with $f = 0.015$. The major-to-minor axis ratio is indicated on the curves. Full curves—MG theory; dashed curves—effective-medium theory. The experimental curve is also shown.

10 Å was used.[14] The full curves were calculated using the MG dielectric constant (10) and the dashed curves using the effective-medium dielectric constant (15). For spherical aggregates, and for spheroidal aggregates of small eccentricity, the calculated absorption is again lower by about two orders of magnitude than the experimental one. For elongated clusters, the absorption rises considerably, but still remains low in comparison with the experimental curve. For small eccentricities the MG and effective-medium theories yield very similar results. For elongated aggregates, the effective-medium theory values are higher and closer to the experimental data. The full curve labeled ∞ corresponds to Simanek's model (MG theory and cylindrical cluster shape), except that he has assumed that the formation of the oxide layer increases the outer radius of the sphere, whereas we assume that the oxide layer builds up at the expense of the metallic core, so that the outer radius remains constant.

We have also performed calculations for larger Al spheres, of diameter 375 Å and with $f = 0.04$, corresponding to one of the samples used by Tanner *et al.*[1] For isolated spheres the calculated absorption is again far too low. The results for aggregated spheres are shown in Fig. 3. The huge differences between the results of the MG and effective-medium theories are due to the large value of ϕ for this sphere size. Whereas the MG theory results are far too low, even for infinite cylinders, the effective-medium-theory values are close to the experimental data if the major-to-minor axis ratio is taken to be of the order of 30. The reason for the complete failure of the spherical-cluster model and the relative success of the cylindrical-cluster model is that for the latter geometry one of the depolarization factors tends to zero. Thus, very flat oblate-spheroidal clusters (which have two small depolarization factors) would have served equally well. It can be concluded that strong far-infrared absorption, of the order of the experimentally observed one, is compatible with the presence of elongated chainlike clusters or flattened disklike clusters (or a mixture of both).

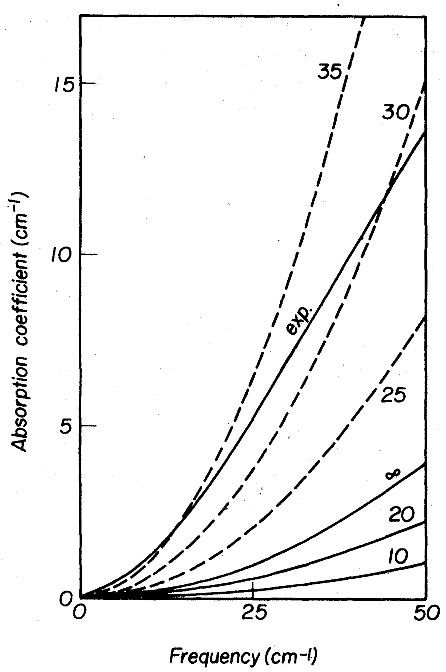

FIG. 3. Same as Fig. 2, but for sphere diameter of 375 Å and $f = 0.04$.

Figure 3 shows that for large particles the frequency dependence of the absorption coefficient calculated by using the effective-medium-theory dielectric constant is steeper than that observed experimentally. This is related to the fact that for the case of large particles (those for which $\phi \geq \frac{1}{3}$) the effective-medium theory predicts metallic behavior of the aggregate dielectric function. However, the particle aggregates studied experimentally[1 2] probably do not exhibit percolation, since every particle is coated by an insulating oxide layer. Another factor which, at the present stage, precludes a clear-cut choice between the MG and the effective-medium theory (or other available formulations[15]) is the large uncertainty in the value of the constant a in Eq. (9), which has not yet been determined experimentally.

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