Far-Infrared Absorption of Silver-Particle Composites

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The far-infrared absorption of oxide-coated small Ag particles in a Teflon insulating host has been measured. Excellent agreement between the experimental absorption and the Maxwell-Garnett theory is obtained when the particle size distribution and oxide coating are taken into account. We show for the first time experimental evidence that a highly absorbing oxide coating will enhance the electric-dipole absorption. Moreover, we explicitly show that the anomalous absorption of oxide-coated Ag particles is mainly due to clustering.

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The study of metal-particle composites has been conducted for many decades.[1-13] An intriguing result found in previous investigations[1-3] of dilute mixtures of small metal particles embedded in an insulating host is that the system appears to have a far-infrared absorption larger than the prediction of simple classical theories by one to several orders of magnitude. A recent experimental study done by Curtin *et al.*[4] showed that such an anomalous enhancement can be qualitatively explained by the clustering of the particles. Though carried out on a different class of system, the experimental work of Devaty and Sievers[5] also suggested that the large absorption is a multiparticle effect.

In this paper, we report far-infrared measurements on oxide-coated Ag particles inside a Teflon host. Measurements on samples containing both well-separated and clustered particles, as determined by a scanning transmission electron microscope (STEM), are presented and compared with the Maxwell-Garnett theory (MGT). Excellent agreement between data on well-separated particles and theoretical calculations is obtained when we include the particle size distribution and the effect of the oxide coating. We show for the first time experimental evidence that a highly absorbing oxide coating plays an important role in the enhancement of the electric-dipole absorption. Moreover, we solve the longstanding discrepancy of orders of magnitude difference between theory and experiment by directly comparing the absorption coefficient of well-separated particles with that of clustered particles.

A new insulating host, Teflon, has been used to measure the far-infrared absorption of small Ag particles. Use of the Teflon host (Dupont DLX 6000) is a significant advance in this field for two reasons: First, compared with gelatin or KCl, it is only weakly absorbing in the far-infrared (absorption coefficient < 1.0 cm^{-1} at any temperature), so that the absorption coefficient, α, of the composite can be determined very accurately at any temperature; and second, contrary to KCl, Teflon can be microtomed to prepare the specimen for the STEM. Therefore, like the gelatin used by Devaty and Sievers,[5] Teflon makes it possible to permit superior sample characterization by STEM.

The Ag particles were prepared in the traditional way,[13] i.e., evaporation of Ag in a mixture of 75-vol% argon and 25-vol% oxygen gas. These Ag particles, called "silver smokes," have an oxide coating[14] on the surface and form needlelike clusters. Using 10 Torr as the pressure inside the evaporator, we could get Ag smokes whose arithmetic mean radius, $\bar{a}$, was 450 Å. The particles were mixed with the Teflon powder and then pressed and broken several times by use of a freezer mill operated at 77 K. The mixture was pressed into pellets for far-infrared studies or imbedded in an epoxy and microtomed into slices about 2000 Å thick for characterization by STEM. These processes allowed us to obtain well-separated particles inside the Teflon host as shown in Fig. 1(a). By using one of the traditional mixing methods, i.e., stirring,[15] we prepared another sample with Ag particles obtained from the same evaporation, but found this sample to be composed of many aggregates as shown in Fig. 1(b). (Note that many of the clusters have a needlelike shape.) It appears that the stirring technique cannot overcome the cohesive forces between the Ag particles belonging to the same cluster.

Another interesting experimental fact is that if we use the *traditional* choice of evaporating pressure, i.e., less than 5 Torr,[2] STEM pictures show that Ag particles inside the Teflon form clusters whose typical dimension is about 1 μm. It is possible that the low oxygen pressure does not give an oxide coating sufficiently thick to prevent cold welding.

The room-temperature absorption of the Ag composites was measured between 15 and 90 cm^{-1} by use of a Fourier transform spectrometer with a helium-cooled germainum bolometer. The data for well-separated particles with volume fraction $f = 3\%$ are shown in Fig. 2. The measured size distribution is given in the inset on Fig. 2. To compare these data with theory, we used the MGT[2,3] along the Drude model for the dielectric constant of metal with $1/\tau = v_{F/l} + v_{F/a}$. We used the plasma frequency $\omega_p = 72\,000$ cm^{-1}, the bulk mean-free-path $l = 550$ Å at room temperature, and

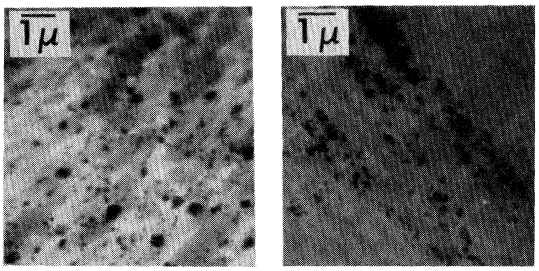

FIG. 1. STEM pictures of Ag particles in Teflon (the volume fraction, f, of Ag is 3%). The Ag particles in both pictures were obtained from the same evaporation. The bar on the figure indicates a length of 1 μm. (a) A sample prepared by use of a freezer mill operated at 77 K. Most of the particles are well separated. (b) A sample prepared by the stirring technique. Many particles form needlelike clusters.

the Fermi velocity $v_F = 1.38 \times 10^8$ cm/sec.[5] The dielectric constant of the Teflon was evaluated as 4.67 from the interference pattern of the high-resolution transmission. At $f << 1$ and $a << \delta$, where δ is the skin depth, low-frequency expansion of the MGT gives $\alpha \propto f\omega^2(\rho + 8\pi^2 a^2/45c^2\rho)$, where ρ is the resistivity of the particles. The first term arises from the induced electric dipoles and the second term comes from the eddy currents due to magnetic dipoles. For typical metal particles, a crossover from electric-dipole to magnetic-dipole absorption is expected at $a \sim 50$ Å. Since the low-frequency calculation does not include the skin-depth effects on the magnetic dipole, we used the complete form[3] of the MGT.

Curve 1 in Fig. 2 shows the calculated absorption coefficient due to electric and magnetic dipoles from MGT using $a = 450$ Å. The ratio of the measured absorption of well-separated particles to the calculated absorption is only about a factor of 3, which is one to several orders of magnitude smaller than the ratios observed by other workers.[1-4] To explain our experimental data quantitatively, we examine the following two mechanisms: (1) particle size distribution[11]; and (2) electric-dipole enhancement due to the oxide coating.[10]

Since the magnetic-dipole absorption increases with the size of the particles, the first mechanism, the particle size distribution, can give an enhancement.[11] However, skin-depth problems prevent the particle size distribution from making a large contribution.[12] If we use the MGT with the size distribution taken into account, MGT(SD), we obtain an absorption coefficient $\alpha = \sum_a \alpha(a) g(a)$, where $\alpha(a)$ is the absorption coefficient from MGT for particles with radius a, and $g(a)$ is the size distribution weighted by its volume. As can be seen in Fig. 2 (curve 2), MGT(SD) shows

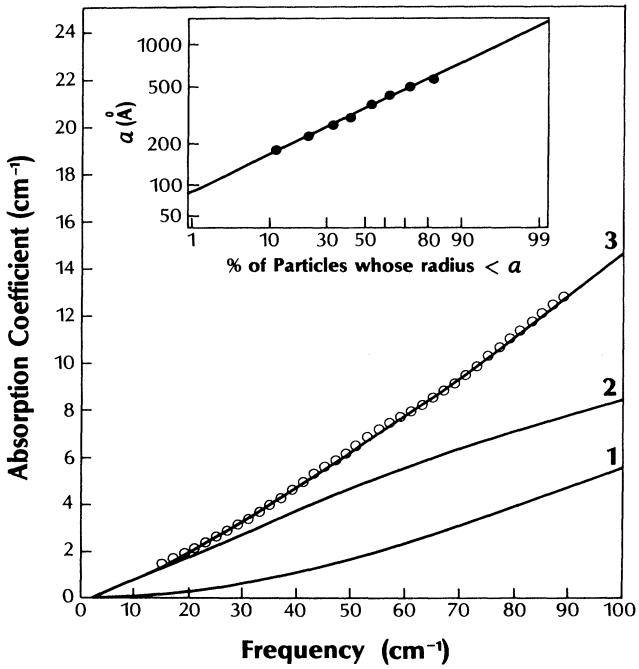

FIG. 2. The frequency dependence of the absorption coefficient of well-separated $f = 3\%$ Ag particles in Teflon. An open circle indicates the experimental data at 300 K. Curve 1 shows the prediction of MGT using the mean particle radius, 450 Å. Curve 2 shows the prediction of MGT after introduction of only the particle size distribution [MGT(SD)]. Curve 3 is obtained from MGT with the particle size distribution and oxide-coating effects included. Inset: Log-probability plot for the size distribution of Ag particles used in our experiment.

an enhancement by a factor of about 2, leaving the ratio between the experiment and theory for these well-separated Ag particles at a factor of 1.5.

We thus considered the second mechanism, i.e., the electric-dipole enhancement due to the oxide coating on the Ag particles. Since the electric-dipole absorption from the MGT is proportional to the resistivity, the electric-dipole absorption can be enhanced if the oxide layer has a large dc resistivity.[10] Therefore, we carried out the MGT calculation taking into account the oxide coating on the particles. For the theory to fit our experimental data of Fig. 2, we need a value for $\rho_c t$ of 1.93 $\Omega \cdot$ cm $\cdot$ Å, where ρ_c is the resistivity of the oxide layer and t is the thickness of the oxide. Using dark-field and bright-field TEM, we found that t for our samples is 24.0 ± 8.0 Å. Therefore, ρ_c can be estimated as 0.08 ± 0.03 $\Omega \cdot$ cm. We performed far-infrared measurements on four other samples, each of which had a different radius and oxide-coating thickness. All of our samples support the above value of ρ_c. The details of this procedure have been published elsewhere.[16]

With the above values, and taking into account the size distribution, the MGT predicts the enhancement of the electric-dipole absorption to be abut 10^3 for our particles. (Refer to curves 1 and 2 in Fig. 3.) For the sample in Fig. 2, the enhanced electric-dipole absorption becomes comparable to the magnetic-dipole contribution above 50 cm^{-1}. However, if $a < 50$ Å, the electric-dipole contribution becomes larger than the magnetic-dipole contribution, and an enhancement of three or four orders of magnitude in the total absorption is possible as a result of the oxide layer.

As can be seen in Fig. 3, the Ag smoke sample in which we deliberately made needlelike clusters (curve 4) shows a large enhancement over the well-separated sample (curve 3). The absorption coefficient of the clustered sample is in agreement with the data taken from Carr *et al.*[2] for Ag particles in KCl with mean radius of 400 Å (curve 5). This shows explicitly that the anomalous absorption observed in Ag smoke is mainly due to clustering.

To explain the "anomalous enhancement," two further mechanisms have been suggested: (3) increase of the paths of eddy currents due to clustering[17]; and (4) electric-dipole enhancement due to the oxide coating and clustering.[7,8,18] We will discuss these two multiparticle effects.

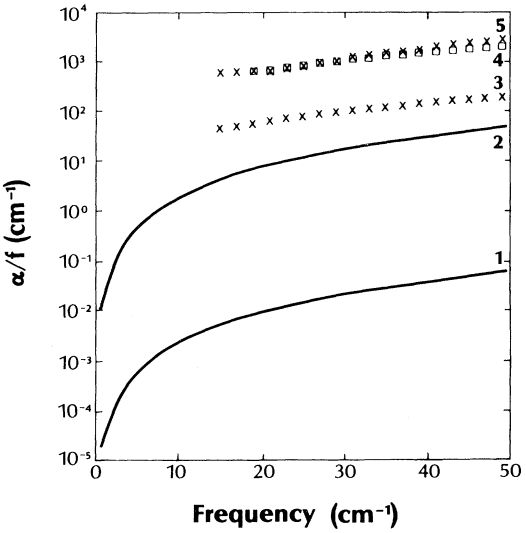

FIG. 3. Frequency dependence of the normalized absorption coefficient. Curve 1 shows the electric-dipole contribution from MGT(SD). Curve 2 shows the calculated electric-dipole contribution enhanced by the oxide layer. A comparison between curves 1 and 2 shows that, according to MGT, the oxide coating will enhance the electric-dipole absorption by 10^3. Curve 3 gives our data for well-separated particles replotted from Fig. 2. Curve 4 gives our data for Ag particles which form needlelike clusters. Note that the clustering gives about a factor of 40 enhancement in absorption. Curve 5 represents data on $\bar{a} = 400$ Å Ag particles in KCl taken from Fig. 3 of Carr *et al.* (Ref. 2). Agreement between curves 4 and 5 strongly suggest that the anomalous absorption of Ag composites is due to the clustering.

Parallel to the absorption measurements on the Ag smoke described in this Letter, we also measured the absorption coefficients of unoxidized Ag particles and found a large enhancement for clustered samples. Our experimental results on the unoxidized Ag particles can be explained by MGT(SD) with the cluster conductivity determined by the surface scattering due to the individual metal particles instead of the cluster itself. If there is no oxide layer, the paths for eddy currents increase as the size of the cluster increases, causing the enhancement of magnetic-dipole absorption. We also applied this model to the experiment done by Devaty and Sievers,[5] and obtained good agreement. The detailed explanations will be published later.[17]

Even though this third mechanism is important for the unoxidized particles, we cannot apply the same mechanism to the enhancement due to the clustering of the metal smoke. The calculation based on the eddy-current argument gives an absorption coefficient less than that of the clustered sample by an order of 1 or 2. Therefore, the mechanism based on the electric-dipole enhancement due to the oxide and the clustering is more plausible to explain the anomalous absorption observed in the Ag smoke.

Nowadays, there are two different theoretical models which predict the electric-dipole enhancement due to the clustering of oxide-coated particles. According to Simanek[7] and Ruppin,[8] a small depolarization factor of needlelike clusters will enhance the absorption by about a factor of 10 over that of the well-separated, oxide-coated particles. However, Curtin and Ashcroft[18] made a new model, i.e., the "cluster percolation model," in which, for clusters near the metal-insulator transition, the electrically coupled metal particles form a tenuous chain and the absorption of such clusters is greatly enhanced relative to single particles. To compare these two models, a more quantitative study on the relation between clusters and the enhancement is required.

From the data presented here and its comparison with MGT(SD), we suggest the following picture regarding the far-infrared absorption of a small-metal-particle composite with low metal volume fraction: Well-separated metal particles *without* oxide coating should have an absorption coefficient given by MGT(SD)[5]; metal particles *without* oxide coating that form clusters should have magnetic dipole absorption enhanced over MGT(SD) as a result of increased eddy current paths[17]; well-separated, oxide-coated particles have an absorption described by MGT(SD) plus an enhancement of the electric-dipole absorption that depends on the resistivity of the coating and its thick-

ness[16]; and clusters of oxide-coated particles have an additional geometry-dependent enhancement over the absorption of unclustered oxide-coated particles.[4,7,8,18]

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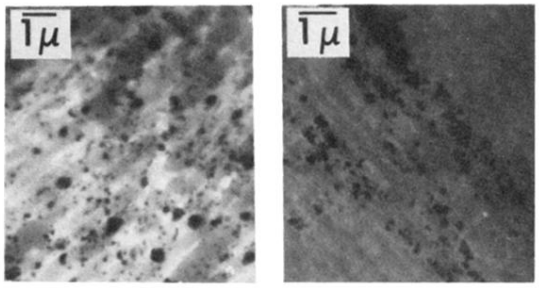

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