Far-Infrared Absorption by Small Metal Particles

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Measurements of the far-infrared absorption coefficient of a novel composite material that can also be studied by transmission electron microscopy permit new bounds to be placed on the anomalous enhancement by well-dispersed small metal particles. Clumped particles are stronger absorbers.

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The anomalous enhancement by many orders of magnitude of the measured far-infrared absorption coefficient of composite materials containing very small metal particles (diameter ≤ 100 Å) with respect to the predictions of simple models is not understood largely because of a lack of well-characterized samples with controllable properties. The configuration of the particles in the samples used in previous investigations, typically a free-standing metal smoke[1] or a metal smoke mixed with an alkali halide and pressed into pellets,[2,3] was not determined, e.g., with an electron microscope. Thus, the available data do not convincingly support or eliminate either proposed explanations that require clumping[4] or intrinsic mechanisms that can take place in isolated particles.[5]

This Letter reports results of measurements on a novel composite material—100-Å-diam Ag particles imbedded in a gelatin matrix. For the first time, the particles under study by far-infrared spectroscopy can also be examined *in situ* by transmission electron microscopy. Samples containing either well-dispersed or agglomerated particles can be prepared. The volume fraction of Ag can be varied over a large range. The experimental far-infrared absorption data are consistent with the Bruggeman[6] model. Thus, the absorption coefficient of materials with well-dispersed particles is not enhanced by several orders of magnitude, if at all. However, samples containing deliberately agglomerated particles are measured to be stronger absorbers.

A Ag hydrosol was prepared by reduction of $AgNO_3$ according to the recipe of Carey Lea.[7] The appropriate amount of gelatin to obtain the desired volume fraction of Ag in the composite was added. The gelatin was cross linked with glutaraldehyde to facilitate sectioning. The water was removed by successive dilutions with acetone or by freeze drying. The material was pressed into pellets for spectroscopic studies or imbedded in an epoxy and sectioned with an ultramicrotome into 500–1000-Å-thick slices for transmission electron microscopy. If clumped particles were desired, a monovalent salt was added to the sol before the gelatin. Further details on sample preparation will be published.

The volume fraction f of Ag in the material was determined by potentiometric titration.

The absorption coefficient was measured from 2 to 25 cm^{-1} by Fourier transform spectroscopy using a lamellar grating interferometer[1] and a cryostat[1] with a ^{3}He-cooled bolometer. The samples were immersed in liquid He ($T = 4.2$K). An insert that permitted up to five samples to be rotated into the light path in turn was used. The absorption coefficient was independent of both temperature ($1.2 < T < 25$ K) and magnetic field ($0 \leqslant H \leqslant 60$ kG).

Figure 1(a) shows a typical electron micrograph of low f freeze-dried material. The particles are well dispersed. Micrographs of material with large f are more difficult to interpret because the particles are densely packed and damage from the electron beam is more difficult to avoid. Figure 1(b) shows Ag particles from the same batch of Carey Lea sol that were deliberately agglomerated with use of sodium citrate. Although beam damage (e.g., coalescence of the particles) has occurred and sodium citrate obscures the view, clumping is evident.

The data are compared with the Bruggeman model,[6] which treats the metal particles and host dielectric on an equal footing. Both the electric and magnetic dipole terms are included, as they are of comparable importance in the far infrared. Although the Maxwell-Garnett[8] model is more appealing on the basis of topological considerations,[9] the Bruggeman model was chosen because it predicts the large increase in absorption at the insulator-metal transition that is expected for densely packed particles and observed experimentally. The Ag particles were modeled[10] as Drude Ag with plasma frequency $\omega_p = 9.0$ eV and Fermi velocity $v_F = 1.39 \times 10^8$ cm/sec. The relaxation time due to boundary scattering was taken as $\tau = x/2V_F$ with the particle diameter $x = 100$ Å. The effect of

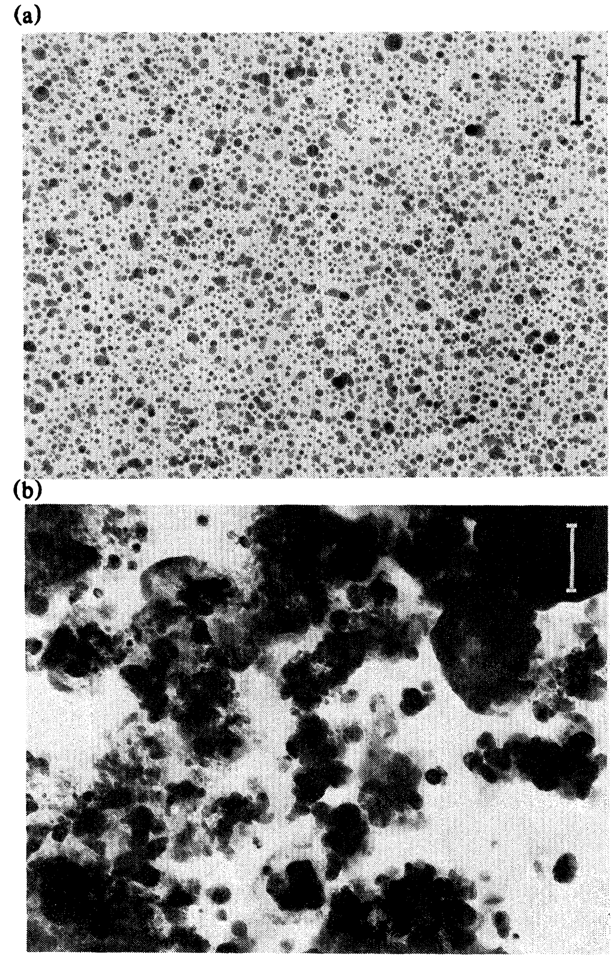

FIG. 1. Transmission electron micrographs of freeze-dried Ag in gelatin. The Ag particles in both pictures are from the same batch of Carey Lea sol. The bars indicate 1000 Å. (a) $f = 0.059$. The dark areas are the particles which are well dispersed. (b) $f = 0.011$. Sodium citrate was added to the sol to induce agglomeration. The dark areas are Ag particles and sodium citrate; the light areas are gelatin and/or epoxy. Some coalescence of the particles has occurred due to beam damage, but clumping is evident.

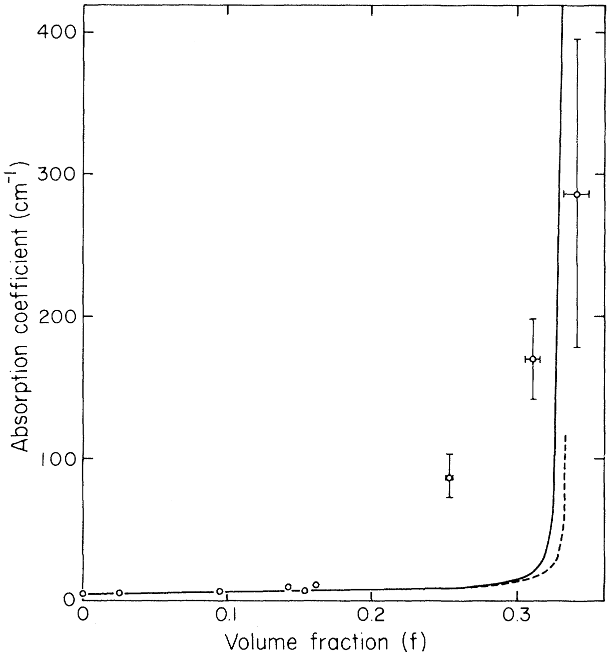

FIG. 2. Volume-fraction dependence of the absorption coefficient of acetone-dried Ag in gelatin at $\tilde{\nu} = 15$ cm^{-1}. Circles indicate the data. The solid (dashed) line shows the prediction of the Bruggeman model for 100-Å-diam Drude Ag particles (particles of a perfect conductor) in gelatin.

a distribution of sizes is negligible and hence was not included in the calculations. The dielectric function of gelatin over $3 < \tilde{\nu} < 25$ cm^{-1} was modeled by $\hat{\epsilon}_0 = \epsilon_{01} + iC\tilde{\nu}^2$, where $\epsilon_{01} = 3.3$, $C = 3.61 \times 10^{-4}$ cm^2, and $\tilde{\nu}$ is the frequency in inverse centimeters. ϵ_{01} was determined from secondary maxima in the interferograms due to multiple reflections of the light by the flat parallel surfaces of the pressed pellets. Then C was obtained from the measured absorption spectrum.

Figure 2 shows the volume-fraction dependence of the absorption coefficient $\alpha(\tilde{\nu} = 15$ cm$^{-1})$ for acetone-dried material. Also shown are the predictions of the Bruggeman model for Ag in gelatin and for particles of a perfect conductor in gelatin. For the latter curve, the absorption is due entirely to the gelatin. Thus, the Bruggeman model predicts that absorption by the Ag particles is dominated by the gelatin unless $f > 0.3$. Theory and experiment are in excellent agreement for $f \lesssim 0.15$. However, the implications regarding the anomalous enhancement must be considered carefully. Although for small f the data are consistent with no enhancement whatsoever, one can only place bounds on the enhancement because the gelatin absorption dominates.

A bound on the enhancement can be estimated by two different arguments. First, consider Fig. 3, which shows the frequency dependence of α/f, a measure of the absorption per particle for Ag in gelatin, obtained by subtraction of the gelatin absorption from the spectrum of Ag in gelatin for $f = 0.154$. Note that this procedure provides only an estimate of the contribution of the Ag particles because properties of the components do not simply add for the effective medium. Also shown are data for Ag particles in KCl (Ref. 3) and the prediction of the Bruggeman model for Drude Ag in KCl for

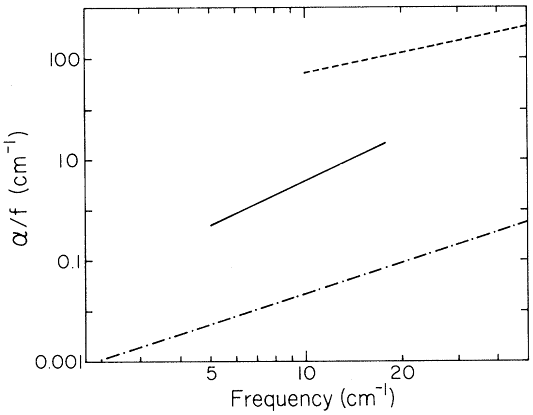

FIG. 3. Frequency dependence of the far-infrared absorption coefficient normalized by f. The solid line was obtained by subtracting the gelatin absorption from the data on Ag in gelatin with $f = 0.154$. The dashed line represents data on a pressed pellet of Ag particles in KCl taken from Fig. 3 of Carr *et al.* (Ref. 3). The dashed-dotted line shows the prediction of the Bruggeman model for 100-Å Drude Ag particles in KCl. Note that the data on Ag in gelatin are only two orders of magnitude larger than theory.

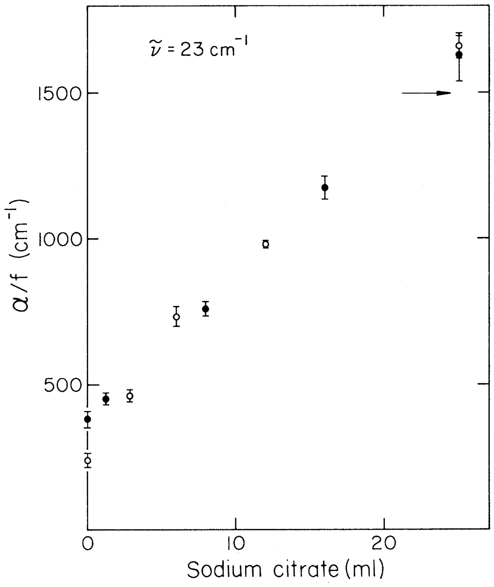

FIG. 4. Normalized absorption coefficient vs degree of clumping. Clumping is measured by the volume of sodium citrate solution added to the sol for freeze-dried Ag particles in gelatin. For these samples, $f < 0.05$. The open and closed circles represent data for two different batches of Carey Lea sol. Clumped particles are stronger absorbers of far-infrared radiation. Since absorption by the gelatin dominates that of well-dispersed Drude Ag particles by two to three orders of magnitude for $f < 0.05$, the actual enhancement due to clumping could be greater than 10^3. The arrow indicates α/f for Ag particles in KCl taken from Fig. 3 of Carr *et al.* (Ref. 3).

small f. Theory and experiment disagree by about four orders of magnitude for Ag in KCl, but the bound on Ag particles in gelatin is only a factor of about 100. Second, note that the electric dipole term of the absorption coefficient for particles of Drude Ag for small f is proportional to $1/\tau$, where τ is the electron relaxation time in the particle. Thus, the absorption by the modeled particles can be artificially increased by increasing the scattering rate in the Drude model. τ must be reduced by a factor of 100 to increase the absorption by the model Ag particles sufficiently to produce a noticeable contribution over the gelatin absorption. Therefore, for well-dispersed Ag particles in gelatin with $f < 0.15$, the far-infrared absorption coefficient is enhanced by a factor of 100 at most, and the data are consistent with no enhancement whatsoever.

According to Fig. 2, the enhancement for Ag-gelatin data over theory, which occurs near $f = 0.3$, is only about a factor of 10. For $f > 0.2$, the frequency dependence of the measured absorption spectrum differs from the cubic dependence of gelatin. Thus, absorption by the Ag particle dominates. This result can be interpreted either as a true enhancement or as evidence for the failure of the Bruggeman model for large f.

The percolation threshold for this silver-gelatin composite at 4.2 K as indicated by dc resistivity measurements is $0.25 < f_c < 0.31$. The large value of f_c attests to the quality of the dispersion. For comparison, $f_c = 0.20$–0.22 for the dielectric constant of pressed pellets of Ag smoke in KCl.[11]

Sodium citrate dissolved in water was added to portions of Ag sol to induce agglomeration of the particles. Figure 4 shows the effect of clumping on $\alpha(\tilde{\nu} = 23\ \mathrm{cm}^{-1})/f$ for samples with $f < 0.05$. The normalized absorption is a factor of 5.3 larger for the samples to which the most sodium citrate has been added. Control samples containing only gelatin and sodium citrate do not show increased absorption with added sodium citrate. Perhaps coincidentally, the largest value of α/f is comparable to the value for Ag particles in KCl.[3] Hence, agglomerated particles are stronger absorbers of far-infrared radiation. For the values of f for the samples used to obtain these data, the absorption by gelatin dominates that of Drude Ag by two to three orders of magnitude. Therefore, the actual enhancement due to clumping could be greater than 10^3.

In conclusion, measurements on the Ag-gelatin composite material demonstrate that the far-infrared absorption coefficient of well-dispersed metal particles is not enhanced by more than 10^2, and perhaps not at all, with respect to the predictions of classical effective-medium theories. Experiments on deliberately agglomerated particles reveal enhanced absorption.

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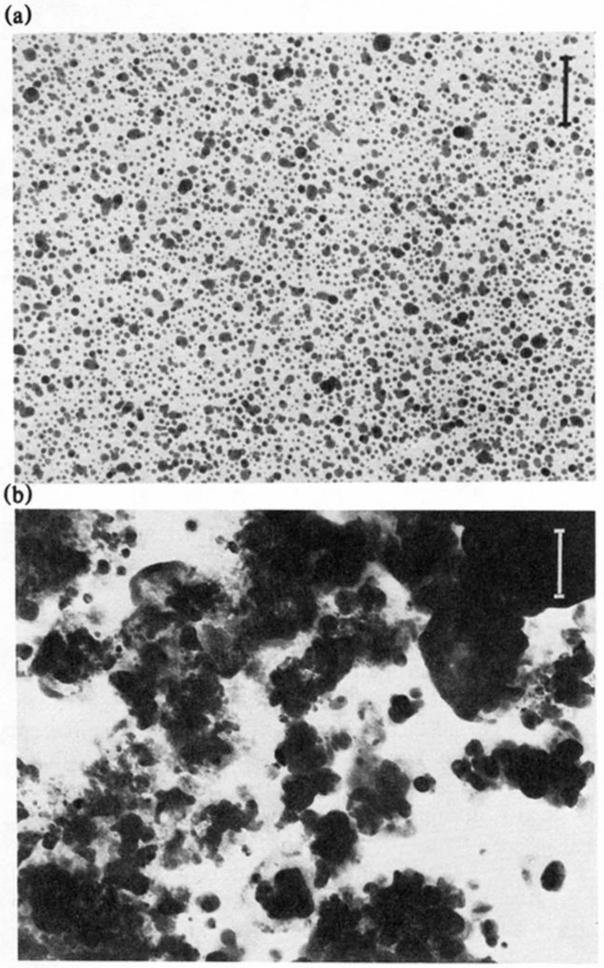

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