Comments

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Comment about the far-infrared absorption by small particles

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(Received 8 November 1983)

It is shown that the agreement between measurements of the far-infrared absorption by small-palladium-particle composites and recently published calculations which used a size-distribution-dependent effective dielectric function was caused by the use of a low-frequency expansion for the magnetic dipole absorption at frequencies where this expansion was no longer valid. When the complete magnetic dipole absorption is used, theory predicts an absorption substantially smaller than is observed.

In a recent Brief Report, Chýlek, Boice, and Pinnick[1] (CBP) discussed the far-infrared absorption by small metal particles. Earlier studies[2-6] had shown that the magnitude of this absorption is more than ten times larger than the predictions of classical electromagnetic theory, even though the classical theory gives correctly the frequency, size, and concentration dependence of the absorption.[7] As was discussed recently by Sen and Tanner,[8] extrinsic mechanisms, such as the effects of clustering and absorption in oxide coatings, also could not predict the magnitude of the absorption while retaining the proper frequency dependence. In their model, CBP used an extension (due to Chýlek and Srivastava[9]) of the dynamic effective-medium approximation[10] (DEMA) which included a distribution of particle sizes. When evaluated in the long-wavelength, low-frequency limit, this model gave an effective absorption coefficient in good agreement with the measured absorption coefficient of 1-μm-radius Pd particles embedded at low volume fraction in KCl.[4] CBP concluded that the anomalous absorption could be explained by assuming a wide distribution of particle sizes.

The purpose of this Comment is to discuss conditions which must be met before the model used by CBP is valid and to make a direct comparison with experiments. Chýlek and Srivastava[11] have also recently discussed the conditions necessary for the model of CBP to be valid. The first condition (the "long-wavelength" limit) requires that the external wavelength be large compared with the particle size. The important parameter here is $k_0 r$, where r is the particle radius and k_0 is the wave vector of the light in the medium surrounding a particle. This wave vector is defined to be

$$k_0 = \frac{\omega}{c}\sqrt{\epsilon_{\text{eff}}} \ , \tag{1}$$

where ω is the angular frequency of the light and ϵ_{eff} is the effective dielectric constant of the composite. The significance of the long-wavelength limit, $|k_0|r \ll 1$, is that the fields to which a particle is subjected may be regarded as spatially uniform, so that only dipole modes are excited and scattering may be neglected. This limit is easily satisfied by all of the far-infrared studies,[2-6] for which $\omega/2\pi c \approx 10$ cm^{-1}, $\epsilon_{\text{eff}} \approx \epsilon_{\text{KCl}} \approx 4.8$, and $r \leq 10^{-4}$ cm$(=1\ \mu\text{m})$, making $|k_0|r \leq 10^{-2}$.

The second condition (the "low-frequency" limit) requires that the electromagnetic skin depth be large compared with the particle size. In this case the important parameter is kr, where k is the wave vector of light "inside" the particle. This quantity is defined by

$$k = \frac{\omega}{c}\sqrt{\epsilon_{\text{met}}} \ , \tag{2}$$

where ϵ_{met} is the complex dielectric function of the particle. By the usual definition that the skin depth δ is the decay length of the electric field amplitude, $\delta = 1/\text{Im}(k)$. The second condition, $|k|r \ll 1$, is *not* always satisfied because the far-infrared dielectric function of metal particles can be extemely large. For example, the Drude dielectric function is

$$\epsilon_{\text{met}}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\omega/\tau} \ , \tag{3}$$

where ω_p is the plasma frequency and τ the electronic scattering time. Together, ω_p and τ determine the dc conductivity, $\sigma_1(0) = \omega_p^2\tau/4\pi$. If $r \approx 10^{-4}$ cm, $\sigma_1(0) \approx 10^6$ Ω^{-1} cm^{-1}, and $\omega/2\pi c \approx 10$ cm^{-1}, then $\epsilon_{\text{met}} \approx i \times 10^7$ and $|k|r \approx 10$. Only when $r \leq 100$ Å$(=10^{-6}$ cm), so that $|k|r \leq 10^{-1}$, does the low-frequency limit become a valid approximation. See also the discussion of Ref. 11.

Magnetic dipole absorption is strongly affected by the skin effect.[4] This absorption enters the DEMA through the first magnetic (TE) Mie coefficient[10,12] which in the long-wavelength limit is

$$b_1 = \frac{1}{3i}(k_0 r)^3\left[\frac{3}{(kr)^2} - 1 - \frac{3}{kr}\cot(kr) - \tfrac{1}{15}(k_0 r)^2\right] \ . \tag{4}$$

If the low-frequency limit is valid, $|k|r \ll 1$, and

$$b_1 = \frac{1}{45i}(\epsilon_{\text{eff}})^{3/2}\left[\frac{\omega r}{c}\right]^5 (\epsilon_{\text{met}} - \epsilon_{\text{eff}}) \ . \tag{5}$$

Equation (5) is identical to Eq. (3) of Ref. 9 and was used by CBP in the second term of their first equation.

A comparison between the low-frequency expansion and the complete expression is most easily[13] made by using the Maxwell-Garnett theory (MGT) to calculate the effective dielectric function and permeability of the randomly inhomogeneous medium. As discussed in Refs. 4 and 10, the MGT, the effective-medium approximation, and the DEMA all predict identical values for the absorption coefficient so long as the metal volume fraction f is small compared with the critical concentration for percolation, f_c. Because the samples studied in the far infrared[2-5] typically had $f \leq 0.03$ while[14] $f_c \approx 0.20$, they are described well by the MGT.

According to the MGT, the absorption coefficient of the composite is

$$\alpha = 2\frac{\omega}{c}\sqrt{\epsilon_{\mathrm{MGT}}\mu_{\mathrm{MGT}}} \ , \tag{6}$$

where ϵ_{MGT} and μ_{MGT} are, respectively, the MGT expressions for the effective dielectric function and permeability of the randomly inhomogeneous medium. If the metal particles are assumed to be spheres embedded at volume fraction f in an insulating host, then the dielectric function is

$$\epsilon_{\mathrm{MGT}} = \epsilon_{\mathrm{KCl}} + \epsilon_{\mathrm{KCl}}\frac{3f(\epsilon_{\mathrm{met}} - \epsilon_{\mathrm{KCl}})}{(1-f)(\epsilon_{\mathrm{met}} - \epsilon_{\mathrm{KCl}}) + 3\epsilon_{\mathrm{KCl}}} \ . \tag{7}$$

Here, ϵ_{met} is the dielectric function of the metal, a Drude dielectric function [Eq. (3)], and ϵ_{KCl} is the dielectric function of KCl, a real and constant dielectric function.

Magnetic dipole (or eddy current) absorption is the dominant far-infrared absorption mechanism by small particles with radii above about 50 Å. This effect, which causes the medium to have a nonzero magnetization even though the constituents are nonmagnetic, has been discussed by Tanner, Sievers, and Buhrman,[2] Russell, Garland, and Tanner,[4] Carr *et al.*,[5] and Stroud and Pan.[10] An expression analogous to Eq. (7) may be derived for the MGT permeability:

$$\mu_{\mathrm{MGT}} = 1 + \frac{3f(\mu_{\mathrm{met}} - 1)}{(1-f)(\mu_{\mathrm{met}} - 1) + 3} \ . \tag{8}$$

In writing Eq. (8), the permeability of the insulating host has been set to unity. The permeability of the small metal particles[15] is related to their magnetic polarizability in the usual way:

$$\mu_{\mathrm{met}} = 1 + \frac{4\pi\gamma_m}{1 - (4\pi/3)\gamma_m} \ . \tag{9}$$

The polarizability is, in turn, proportional to the first magnetic Mie coefficient b_1, given in Eq. (4) and (at low frequencies) Eq. (5):

$$\gamma_m = \frac{9i}{8\pi}\frac{b_1}{(k_0 r)^3} \ . \tag{10}$$

The absorption coefficient of the inhomogeneous medium is calculated by using Eq. (3) for the dielectric function of the metal particles, Eqs. (6)–(10), and either Eq. (4) for the general case or Eq. (5) at low frequencies.

Figure 1 presents the measured absorption coefficient of $r = 1$ μm Pd particles[4] at a volume fraction of 0.01 in KCl. The dashed line shows a fit to these data using the MGT with the magnetic dipole absorption calculated from the

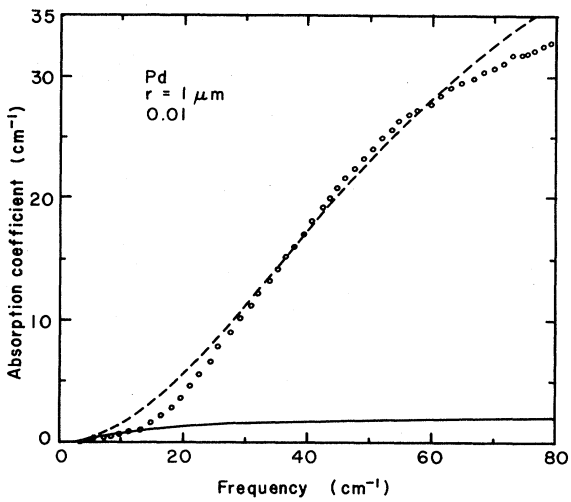

FIG. 1. Far-infrared absorption by a Pd/KCl composite system (from Ref. 4). The dashed line shows the absorption calculated when the low-frequency expansion for the magnetic dipole absorption is used while the solid line shows the absorption calculated from the complete expression. The parameters used in the model are the same for both curves.

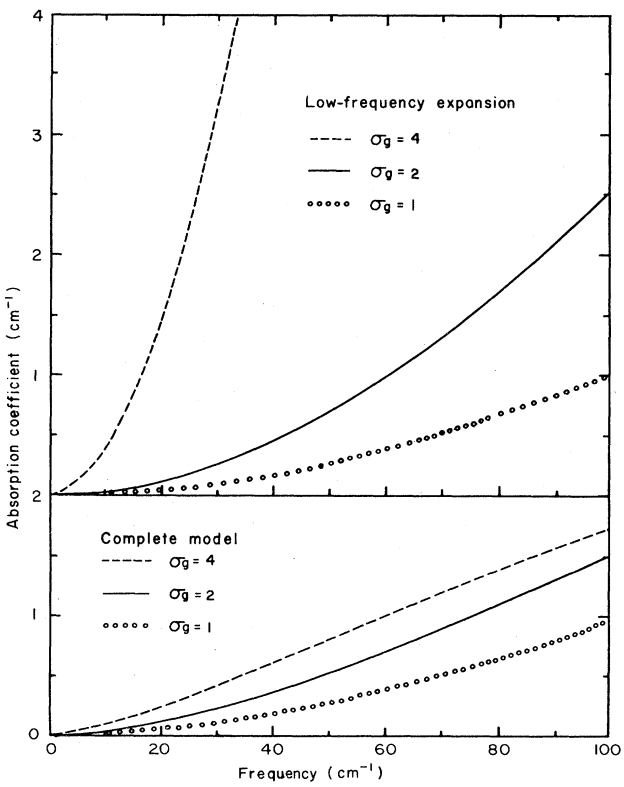

FIG. 2. Calculated absorption coefficient for a small-particle composite, illustrating the effect of a particle size distribution on the absorption. The upper panel shows the absorption when the low-frequency expression is used in the calculations while the lower panel gives the result of the complete theory. Curves are shown for a log-normal distribution with geometric standard deviations of 1 (δ function), 2, and 4. Median particle radius is 300 Å.

low-frequency expansion, Eq. (5). The single adjustable parameter in this fit was the particle radius r. [Because Eq. (5) gives an r^2 variation to the absorption, the radius is a convenient parameter. I could also have varied the conductivity or the scattering time.] The other quantities used were the same as those of Russell *et al.*:[4] $f=0.01$, $\omega_p=50\,000\ \mathrm{cm}^{-1}$, $1/\tau=500\ \mathrm{cm}^{-1}$, and $\epsilon_{\mathrm{KCl}}=4.8$. The best fit was obtained with $r\approx 0.2\ \mu\mathrm{m}$, a factor of 5 smaller than the actual size. This result is not correct, however, because the parameter which was assumed to be small in making the low-frequency expansion, $|k|r$, is in this case *not* small; it varies from $|k|r=0.5$ at 4 cm^{-1} to $|k|r=2.4$ at 80 cm^{-1}. The solid line in Fig. 1 shows the absorption coefficient when the complete expression for the magentic dipole absorption, Eq. (4), is used in the calculation. At very low frequencies this curve is the same as the low-frequency expansion (as expected!) but, once $|k|r$ approaches unity, the calculated absorption coefficient saturates at a low value of $\alpha\approx 2\ \mathrm{cm}^{-1}$, more than a factor of 10 smaller than the experimental absorption. Coincidentally, the 0.2-μm (2000 Å) radius is close to the size where the absorption coefficient as a function of particle size is a maximum.[4] Therefore no choice of parameters in the complete theory can improve significantly the agreement with experiment.

CBP and Chýlek and Srivastava[11] found that including a wide range of particle sizes in the calculation enhanced the absorption. This enhancement is not enough to explain the experimental data. As an example, I have shown in Fig. 2 the calculated absorption coefficient for several size distributions. The median particle radius was taken to be 300 Å; otherwise, the same parameters as for Fig. 1 were used. The particle size distribution was assumed to follow a log-normal distribution with geometric standard deviations of 1 (δ function distribution), 2, and 4. (The measured distributions[14,16] of small metal particles typically have a geometric standard deviation of 1.5–2.) The upper panel shows the absorption when the low-frequency expansion is used. In this case, the rapid increase in absorption with the distribution width is caused by a combination of the r^2 variation of the absorption and the shape of the log-normal distribution. The lower panel gives the absorption calculated from the complete equation. Here, the relatively small absorption increase is due to the fact that at each frequency there is maximum absorption at some particular size; broadening the distribution makes more of the particles fall into that size range. (For a while, at least; if the distribution were to become too broad, the absorption would be reduced because too few particles fell into the range for high absorption.) This increase in absorption, however, is only about a factor of 2 to 3 and is insufficient to make experiment and theory agree.

In summary, the recent calculation of CBP, in which the anomalous magnitude of the far-infrared absorption by small-particle composites was attributed to a size distribution for the metal particles, is incorrect. This error has also been noted by Chýlek and Srivastava.[11] The low-frequency expansion for the magnetic dipole absorption is not valid at far-infrared frequencies for sizes above 100 Å. The far-infrared absorption by small metal particles thus remains a mystery.

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[11]Petr Chýlek and Vandana Srivastava, Phys. Rev. B **30**, 992 (1984) (this issue).

[12]See, for example, H. C. van de Hulst, *Light Scattering by Small Particles* (Wiley, New York, 1957; Dover, New York, 1981).

[13]If the complete expression for the Mie coefficient is used in the size-distribution-modified DEMA, a trancendental integral equation for ϵ_{eff} results. See Eq. (12) of Ref. 9. A numerical evaluation of this model is given in Ref. 11. Note further that the original work of Stroud and Pan (Ref. 10) used also only the low-frequency expansion of the magnetic-dipole term. However, in that paper the absorption was never evaluated for parameter values where the expansion was invalid.

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[15]Being nonmagnetic, the permeability of the metal itself is, of course, very near to unity; Eq. (9) gives the permeability of a magnetic substance which, when made into a small particle, would have the same magnetic polarizability as the small conducting particle. As far at the magnetic dipole absorption is concerned, it does not matter whether the magnetization is due to magnetic small particles or to eddy currents in conducting small particles.

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