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Temperature-dependent far-infrared absorption of silver smoke

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We report measurements of the temperature dependence of the far-infrared absorption of Ag smoke in a Teflon host. By extending the measuring temperature from 298 K down to 4.4 K, we found that the absorption coefficient at 4.4 K is smaller than that at room temperature by only 10%. This slight difference in the absorption coefficient between 4.4 and 298 K proves that the measuring temperature itself is not responsible for the previously observed anomalous enhancement of the far-infrared absorption for these metal-insulator composites. We further suggest an explanation for the temperature dependence of our Ag-Teflon composites based on the electron-impurity scattering mechanism within the Ag particles.

The interaction of metal smokes (small metallic particles produced by the evaporation of metal in a noble-gas–oxygen atmosphere) with electromagnetic radiation has been of interest for more than ten years because of their anomalous far-infrared absorption.[1-11] Many workers[1-4] have measured the far-ir absorption of metal smokes at low temperatures (4.4–20 K) and have found that the measured absorption is enhanced by at least an order of magnitude with respect to the predictions of simple classical electromagnetic models. In some cases, the discrepancy can be several orders of magnitude.

Recently, we reported both far-infrared measurements and electron microscopy studies of Ag smokes dispersed in a Teflon host. This study[5] was done at room temperature. It was the conclusion of this study that the anomalous far-ir absorption of these samples was mainly due to clustering.[6] Even though these results demonstrated clear and direct evidence that the anomalous absorption in our experiment was due to clustering, there remained one question. Was it possible that the samples used by other workers were not clustered (as ours were) and that the anomalous enhancement they observed was due to their much lower measuring temperature? To answer this question, we have measured the temperature dependence of the far-ir absorption of Ag smoke in a Teflon host, an extension of our earlier work at room temperature. Most of the earlier experiments[1-4] by other workers on small-metal-particle composites showed no temperature dependence for the very limited temperature range 4.4–20 K. The experiments reported here cover the much larger temperature range from 298 down to 4.4 K.

The silver smoke used in this work was evaporated in an atmosphere composed at 75 vol% argon and 25 vol% oxygen[7] (total pressure: 35 torr). The metal particles had an average radius of 1250 Å. The smoke was mixed with Teflon powder (DLX6000) using a freezer mill operated at 77 K (Ag volume fraction, $f=3\%$) and pressed into a pellet. Scanning transmission electron microsope (STEM) pictures of our sample showed that the Ag particles were well separated inside the Teflon. The detailed methods of sample preparation and characterization by means of a STEM were described earlier.[8]

At various temperatures (4.4, 77, 155, 265, and 298 K), we measured the transmittance of both our sample and a pure Teflon pellet between 20 and 80 cm^{-1} using a BOMEM DA3.02 Fourier-transform spectrophotometer. We repeated the far-ir measurements as we thermally cycled our samples several times, but could find no hysteresis effects. We obtained the absorption coefficient of the Ag particles by subtracting the contribution of the pure Teflon.[12] In Fig. 1, we present the absorption coefficient,

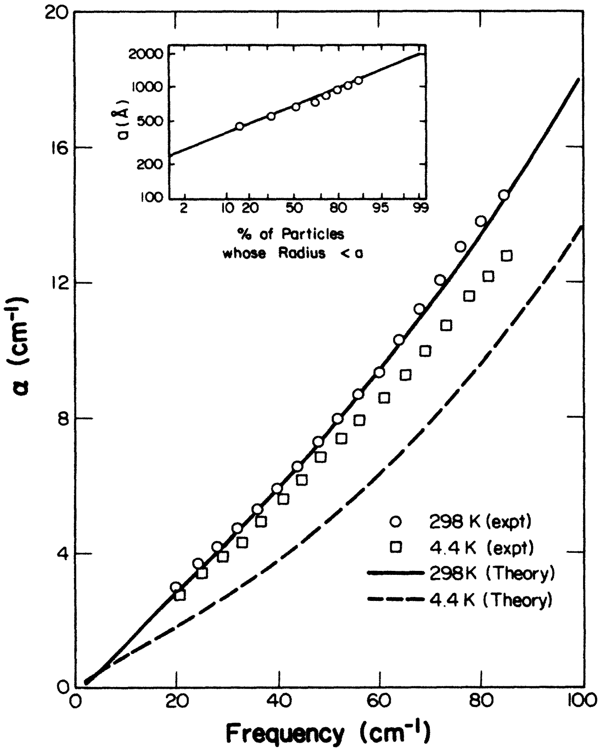

FIG. 1. The frequency dependence of the absorption coefficient of well-separated $f=3\%$ Ag particles in Teflon. The experimental data show that the absorption coefficient decreases by 10% as the temperature drops from 298 to 4.4 K. The MGT predicts a much stronger temperature dependence if the electron-impurity scattering inside the Ag particles is not included. Inset: The size distribution of silver particles follows a log-normal distribution with a volume-averaged radius of 1250 Å.

α, characteristic of the metal particles. For simplicity we present only the coefficients obtained at 4.4 and 298 K since the absorption is observed to be a smooth function of the temperature and for intermediate temperatures, falls between the values shown.

As can be seen in Fig. 1, α actually decreases but only by 10% as the temperature decreases from 298 to 4.4 K. Since the absorption coefficient is only slightly temperature dependent, it is possible to conclude that the different measuring temperature used by other workers[1-4] cannot, by itself, be responsible for the anomalous far-ir absorption they observed. Therefore, as concluded in our earlier paper, clustering of metal particles is the most important mechanism for the enhancement of far-ir absorption[4-6,11] in the temperature range 300–4 K.

From Fig. 1, it is apparent that a temperature change produces a relatively small change in the far-ir absorption of the small metal particles. We will attempt to explain both qualitatively and quantitatively the observed temperature dependence of α of our Ag particles. To explain the observed temperature dependence of our measured absorption coefficients, we will use the Maxwell-Garnett theory (MGT)[13] for sake of simplicity. To include the magnetic dipole absorption, we will use the magnetic permeability arising from induced eddy currents[8,9] in the MGT framework.

Two parameters of importance in the calculation are the dielectric constants of the insulator and metal, respectively. The dielectric constant of the Teflon, ϵ_i, is found to be 4.67 from the interference pattern of the high-resolution transmission.[8] The complex dielectric constant of silver is approximated by the Drude model,

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

with plasma frequency[14] $\omega_p = 72\,000 \ \mathrm{cm}^{-1}$. We consider the total relaxation rate τ^{-1}, to be the sum of the bulk relaxation rate τ_b^{-1} and the surface scattering rate τ_s^{-1},

$$1/\tau = 1/\tau_b + 1/\tau_s \ . \tag{2}$$

The surface scattering of an electron can be represented by the electronic relaxation time, $\tau_s = a/v_F$, where a is the radius of a Ag particle and v_F is the Fermi velocity taken to be $v_F = 1.38 \times 10^8$ cm/sec. Similarly, we take the bulk relaxation time, τ_b, to be equal to l/v_F, where l is the mean free path of pure Ag. Since the surface relaxation mechanism is temperature independent, the temperature dependence of the bulk relaxation time will be responsible for the temperature dependence of the magnetic-dipole absorption.

For $f \ll 1$ and $a \ll \delta$, where δ is the skin depth, a 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. As pointed out by Stroud and Pan,[9] when metal particles have a radius larger than 50 Å, the magnetic-dipole contribution to the far-ir absorption is larger than the electric-dipole contribution. (For our Ag smoke, the magnetic-dipole absorption is higher than the electric-dipole absorption by three or four orders of magnitude.) Since the low-frequency expansion does not include the effect of the skin depth on the magnetic-dipole contribution, we used the complete form of the MGT.[8]

As shown above, the electric-dipole absorption is proportional to the resistivity of the metal particle. Since our Ag smoke was oxide coated, the electric-dipole contribution was enhanced due to the high resistivity of the oxide coating. A simple calculation[8,10] based on the MGT shows that the electric-dipole absorption of the oxide-coated metal particles is given by

$$\alpha = \sum_a \sqrt{\epsilon_i} f \frac{\omega^2}{c^2} \frac{9ct\epsilon_i}{4\pi a} \rho_c g(a) \equiv (B\rho_c t)\omega^2 \ , \tag{3}$$

where ρ_c is the resistivity and t is the thickness of the coating. The quantity represented by B is easily calculated using the volume-weighted size distribution of the Ag particles, $g(a)$. With $\rho_c/\rho = 10^5$ and $t/a = 0.1$, the electric-dipole absorption can be enhanced by four orders of magnitude.

Compared to the large change in the electric-dipole absorption, the inclusion of the oxide-coating effect has a much smaller effect on the magnetic-dipole absorption. Because of the high resistivity of the coating, the power dissipation due to eddy currents inside the oxide coating can be neglected, so we use the reduced value $(a - t)$ instead of a in the MGT. Moreover, the effective volume for the magnetic-dipole absorption will be reduced, so the modified volume fraction, $f^* = f\sum g(a)[(a-t)/a]^3$, is used when we calculate the magnetic-dipole contribution.

The dark-field STEM pictures indicated that the average value of t was 83 ± 17 Å. The size distribution of our silver particles obtained from the STEM is shown as an inset in Fig. 1. By using the Drude model and the known dc conductivity of pure silver at each temperature, we estimated that the bulk mean free path l at 298 K was 520 Å. With these values for the required parameters, we calculated the room temperature absorption coefficient of our composites. As indicated in Fig. 2, we could obtain an excellent fit for the room temperature data using just one adjustable parameter, namely, $B\rho_c t = 1.02 \times 10^{-3}$ cm. The measured value of B and t give $\rho_c = 0.08 \pm 0.03 \ \Omega$ cm. This high resistivity of the oxide coating can produce a large enhancement of the electric-dipole absorption (by three or four orders of magnitude), so the electric-dipole absorption (curve 2 in Fig. 2) of our silver smoke becomes comparable to the magnetic-dipole absorption (curve 1 in Fig. 3).

Following the same line of reasoning, we tried to explain the weak temperature dependence of the measured absorption coefficient of our sample. If there is no impurity scattering inside the Ag particles, the mean free path l will be very large at low temperatures. At 4.4 K, we used l(4.4 K) = 10 000 Å, since the calculated absorption coefficient is insensitive to l if $l \gg 10\,000$ Å. However, using this value, the absorption coefficient calculated at 4.4 K does not agree with the experimental data (refer to Fig. 1). The temperature dependence of the calculated absorption coefficient, while in the correct direction, is too large. This discrepancy might be explained in two ways: (i) the resistivity of the oxide coating is itself temperature dependent, and/or (ii) the electron-impurity scattering of electrons inside the Ag particle must be taken into account.

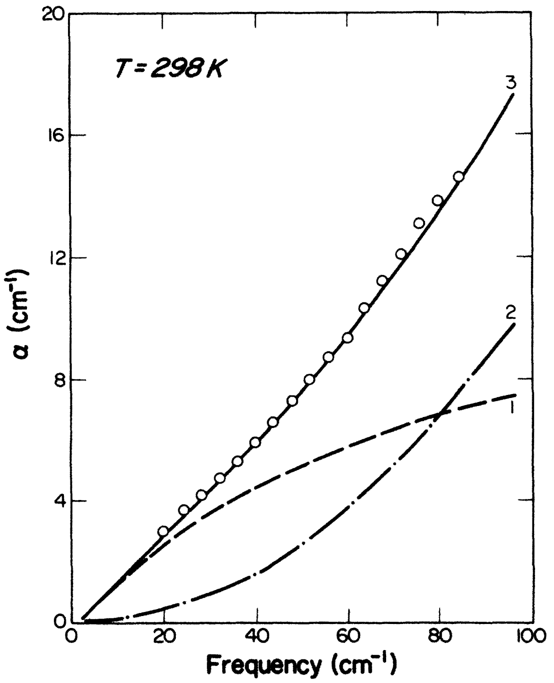

FIG. 2. The room temperature absorption coefficient of a "well-separated particle" Ag smoke, where $f = 3\%$ in Teflon. Open circles: the measured absorption coefficient. Curve 1: the theoretical value for the magnetic-dipole contribution. Curve 2: the theoretical value for the electric-dipole contribution of the oxide-coated Ag particles. Curve 3: the sum of the magnetic- and electric-dipole contributions, curves 1 and 2.

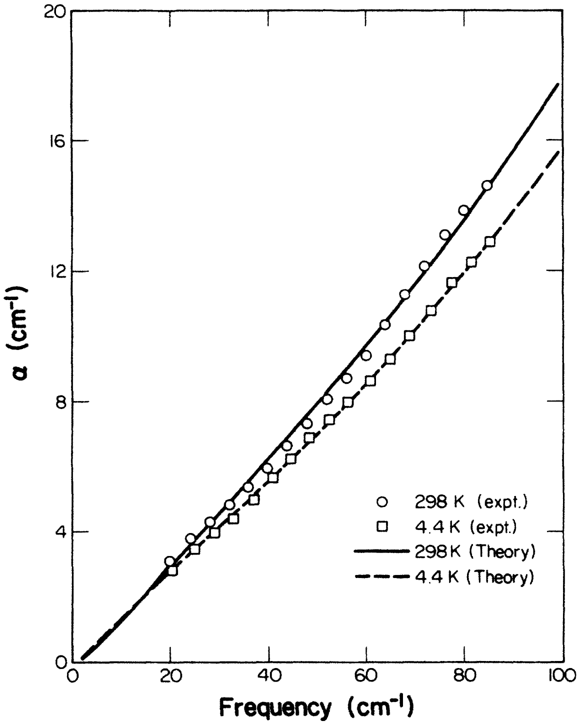

FIG. 3. The frequency dependence of the absorption coefficient of Ag particles (with $f = 3\%$) in Teflon. After introducing the electron-impurity scattering, a two parameter fit to the MGT can provide theoretical predictions which are consistent with our experimental data.

If the resistivity of the oxide coating increases as the temperature decreases, the electric-dipole contribution of the coating will increase, resulting in a *weaker* temperature dependence. Therefore, we tried unsuccessfully to fit our data by varying the value of ρ_c without introducing impurity scattering. For example, with the 4.4 K data, we could not find any single value of ρ_c which, when used with Eq. (3), could explain the absorption coefficient data.

If impurity scattering of the electrons inside the Ag particles is important, then there is an additional contribution to the total relaxation rate,

$$1/\tau = 1/\tau_b + 1/\tau_S + 1/\tau_i \ , \tag{4}$$

where $\tau_i = l_i/v_F$ is the relaxation time for impurity scattering with l_i the appropriate mean free path. The introduction of impurity scattering reduces the relative importance of the bulk relaxation time, so the overall temperature dependence of τ will be weaker.

With a single value of $B\rho_c t = 0.85 \times 10^{-3}$ cm and $l_i = 600$ Å for all temperatures, we were able to obtain a good fit of the theoretical prediction to the experimental data. Figure 3 shows the excellent agreement between the measured absorption coefficients and the calculated one using this two parameter fit. The small value of l_i required to produce this agreement suggests that many impurities are present inside the Ag particles. Since the silver particles used were very pure before the evaporation process, we suspect the impurities were introduced during the evaporation process. Clearly, the number and type of impurities must be a function of the evaporation conditions.

The decreased absorption observed at the lower temperatures can be qualitatively understood by examining the roles of conductivity and skin depth in magnetic-dipole absorption. The low-frequency expansion of the MGT shows that the magnetic-dipole absorption is proportional to the conductivity of the particle. At low temperatures, the bulk mean free path increases and the conductivity of the Ag particles also increases, so the ability to absorb due to the magnetic dipoles will increase. However, as can be seen in Fig. 2, the magnetic-dipole absorption for our Ag-smoke–Teflon composite indicates a strong saturation. This implies that the skin depth is comparable to or smaller than the size of our particles. Therefore, the high conductivity makes the fields penetrate into the Ag particles a progressively shorter distance, so the net absorption will be determined by the competition between an increased ability to absorb and a decreased volume for absorption. The saturation effect due to the skin depth also explains the experimental observation that the observed absorption coefficient has a frequency dependence closer to ω^1 than the expected ω^2, even though the electric-dipole contribution due to the oxide coating shows a ω^2 dependence.

In summary, the temperature dependence of the far-ir absorption coefficient of Ag smoke in a Teflon host has been experimentally determined. A plausible explanation for the weak temperature dependence observed can be obtained by including an additional temperature-independent term for impurity scattering in the electronic relaxation time. Moreover, the weakness of the temperature dependence observed proves that the temperature used for the measurement of the absorption coefficient cannot explain the anomalous enhancement of the far-ir absorption of small-metal composites seen by other workers.

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