FAR INFRARED ABSORPTION IN METAL-INSULATOR COMPOSITES*

N. E. Russell, G. L. Carr and D. B. Tanner
The Ohio State University, Columbus, Oh. 43210

ABSTRACT

The absorption coefficient of composite systems, formed by compacting together small metal particles and finely ground KCl powder, has been measured at far infrared frequencies (4-400 cm^{-1}). The measurements were made on particles of aluminum, prepared by inert gas evaporation, having mean diameters in the range 200 Å to 1000 Å and on particles of palladium, with mean diameter 2 μm. Measurements were made for metal filling factors, f, between 0.001 and 0.10. The absorption coefficient is nearly linear in concentration for small concentrations but rises more rapidly than linearly at larger values of f, indicating the onset of a metal-insulator transition. The dependence of the absorption coefficient on particle size is very weak. A theory which includes eddy current (magnetic dipole) absorption gives a fair description of the data for the largest particles but falls several orders of magnitude below the data for the smallest ones.

INTRODUCTION

In this paper we present results of measurements of the far infrared transmission in composite systems. The specimens studied were made of small metal particles in an insulating matrix. The absorption in such small particle samples has been observed[1,2] to be many orders of magnitude larger than would be predicted by simple theory, for example that of Garnett.[3]

EXPERIMENTAL DETAILS

Aluminum small particles were made by the smoke evaporation method described by Granqvist and Buhrman.[4] Aluminum foil is evaporated from a tungsten filament in the presence of a fraction of a Torr of argon gas. The smoke particles collect on the sides and top of a glass cylinder which surrounds the filament. By varying the argon pressure we have been able to make particle batches with average diameters of 200 Å to 1000 Å, as determined by scanning electron microscopy, and a fairly narrow range of diameters. In addition palladium small particles with average diameter of 2 μm were obtained from a commercial source.[5]

The metal particles were thoroughly mixed with finely ground (40 μm < d < 120 μm) KCl powder and pressed, under vacuum, into a solid disc. The samples were reground and repressed three to five times in an attempt to achieve uniformity. X-ray emission measurements in the electron microscope indicated a fairly uniform spatial distribution of aluminum particles.

The far infrared measurements were made on samples at 4.2 K using lamellar grating[6] (4-40 cm^{-1}) and Michelson (20-200 cm^{-1})

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interferometers in conjunction with a germanium bolometer-detector operating at 1.2 K. From the measured transmission T we calculate the absorption coefficient from

$$\alpha(\omega) = \alpha_0 - \left[\ln T(\omega)\right]/x \qquad (1)$$

where x is the thickness of the specimen and ω is the far infrared frequency. To account approximately for the reflectance of the sample and to compensate for detector nonlinearities α_0 is chosen so that $\alpha(0) \equiv 0$, as it must.

EXPERIMENTAL RESULTS

Figure 1 shows the absorption coefficient for aluminum small particles, d~ 600 Å, between 8 cm^{-1} and 70 cm^{-1} for Al concentrations of 0.003, 0.01 and 0.03 by volume. The data are shown at low resolution. In higher resolution measurements an interference pattern appears at low frequencies due to multiple internal reflections between the plane faces of the sample. From the fringe spacing the index of refraction of the composite system can be obtained. The index so found is larger than that of the pressed KCl by about 10% in the f = 0.03 sample.

The size dependence of the absorption coefficient in these samples is unusual. Both d = 200 Å and d = 800 Å particles have smaller values of the absorption coefficient at a given frequency and concentration than do the d = 600 Å particles. We find $\alpha(200\ \text{Å}) \sim (1/6)\alpha(600\ \text{Å})$ and $\alpha(800\ \text{Å}) \sim (\frac{1}{3})\alpha(600\ \text{Å})$. The shapes of the curves are quite similar.

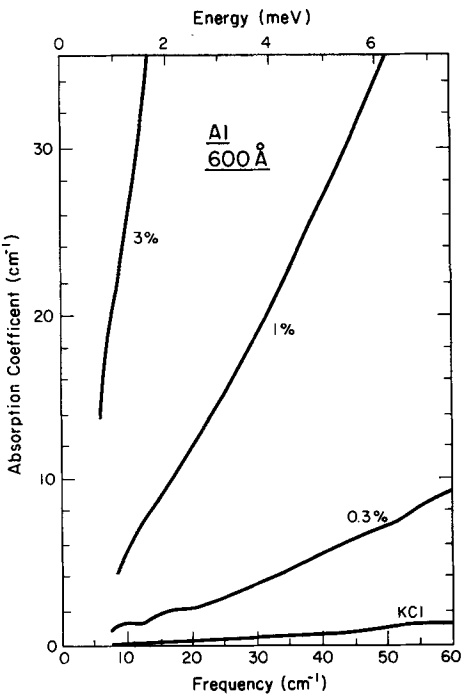

Fig. 1. Absorption coefficient of Al small particles.

Figure 2 shows the absorption coefficient of palladium small particles, d = 2 μm, between 5 and 70 cm^{-1}, for Pd concentrations of 0.001, 0.0029, 0.01, 0.029 and 0.096 by volume, at low resolution. The magnitude of the absorption coefficient is of the same order as the much smaller aluminum particles. However the shape is quite different: there is a tendency towards saturation in α at frequencies above 50 cm^{-1}.

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THEORY

At metal volume fraction $f \leq 0.03$ the Maxwell-Garnett[3] theory (MGT) and effective medium approximation[8] (EMA) for the composite dielectric function give identical values for the absorption coefficient in the far-infrared. The MGT dielectric function is

$$\varepsilon_{MGT} = \varepsilon_i + \varepsilon_i \frac{3f(\varepsilon_m - \varepsilon_i)}{(1+f)\varepsilon_m + (2+f)\varepsilon_i} \quad (2)$$

where ε_m is the dielectric function of the metal and ε_i is that of the insulator. The absorption coefficient is given by $\alpha_{MGT} = \omega\varepsilon_2/nc$ where c is the speed of light, $\varepsilon_2 = \mathrm{Im}(\varepsilon_{MGT})$ and $n = \mathrm{Re}(\varepsilon_{MGT})^{\frac{1}{2}} \simeq (\varepsilon_i)^{\frac{1}{2}}$. If ε_i is constant and ε_m has the Drude form, the calculated absorption coefficient is quadratic in frequency (observed in low frequency experiments) but too small by up to five orders of magnitude. The values are independent of size (on $\alpha \sim 1/d$ at the lowest frequencies if one puts $\tau \simeq d/v_f$, where d is the particle diameter and v_f, the fermi velocity, into the Drude experession.) As an example, using Drude parameters appropriate to aluminum at 70 cm^{-1} $\alpha_{MGT} \sim 0.03\ f\ cm^{-1}$ whereas experiment gives $\alpha \sim (1000\text{-}6000) f\ cm^{-1}$.

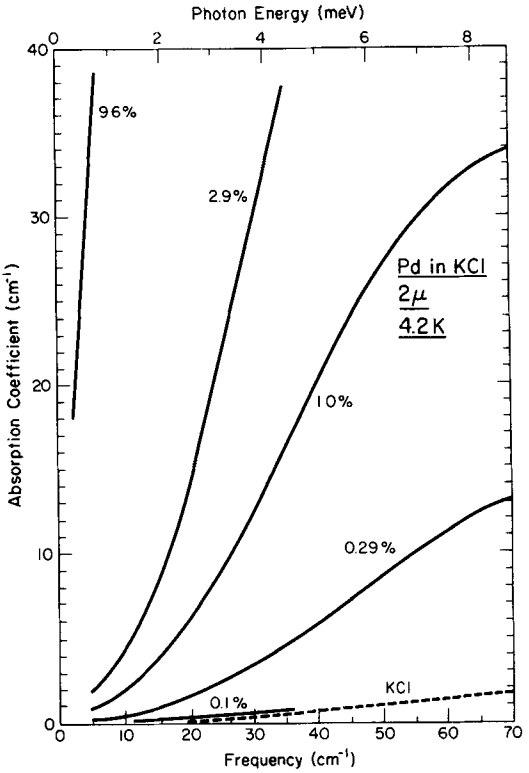

Fig. 2. Absorption coefficient of Pd small particles.

As has been pointed out previously,[1] magnetic dipole (eddy) current losses are larger than the electric dipole losses considered in the simple MGT for metallic particle sizes greater than about 50 Å diameter. A complete theory of this effect has recently been given by Stroud.[9] In an ac field a single spherical small particle has a definite magnetic dipole moment given by[10]

$$\vec{m} = \Omega\gamma\vec{H}_{app} \quad (3)$$

where $\vec{H}_{app}$ is the applied field, Ω is the particle volume and

$$\gamma = -\frac{3}{8\pi}\left[1 - \frac{3}{(ak)^2} + \frac{3}{ak}\cot(ak)\right] \quad (4)$$

is the magnetic polarizibility in which a is the particle radius

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and k is the wave vector of light waves of frequency ω in the particle: $k = \omega(\varepsilon_m)^{\frac{1}{2}}/c$. At low frequencies the absorption is governed by $\mathrm{Im}(\gamma) \simeq a^2\omega\sigma/10c^2$ where σ is the dc conductivity.

To calculate the absorption coefficient of a composite including eddy currents we construct the following argument: from the outside the fields of the dipole described by Equations (2) and (3) are indistinguishable from those of a uniformly magnetized sphere with total dipole moment

$$\vec{m} = \frac{\Omega}{4\pi}(\mu_m - 1)\vec{H}_{in} = \Omega\vec{M} \tag{5}$$

where μ_m is a fictitious permeability, M the dipole moment/unit volume and H_{in} a fictitious internal field. Note that H_{in} would be uniform over the entire particle, whereas because of the skin depth the actual fields inside the particle are not uniform at all. For a spherical particle

$$\vec{H}_{in} = \vec{H}_{app} - \frac{4\pi}{3}\vec{M}$$

and

$$\mu_m = \frac{1 + \frac{8\pi}{3}\gamma}{1 - \frac{4\pi}{3}\gamma}$$

The MGT expression for the composite permeability is of the same form of as Equation (1) with ε replaced by μ. The absorption coefficient is given by $\alpha = 2\omega\kappa/c$ where $\kappa = \mathrm{Im}(\varepsilon_{MGT}\mu_{MGT})^{\frac{1}{2}}$. Figure 3 shows the calculated absorption coefficient for the 2 μm Pd particles. At 70 cm^{-1} the calculation is smaller than experiment by about an order of magnitude. The qualitative shape of the calculation is similar to experiment. The absorption coefficients start out quadratic but the calculations bend over much sooner than do the experimental data. In calculating the curves in Figure 3 we have used Drude parameters appropriate for Pd.[11] Curves closer to experiment can be obtained by treating the Drude parameters as free variables.

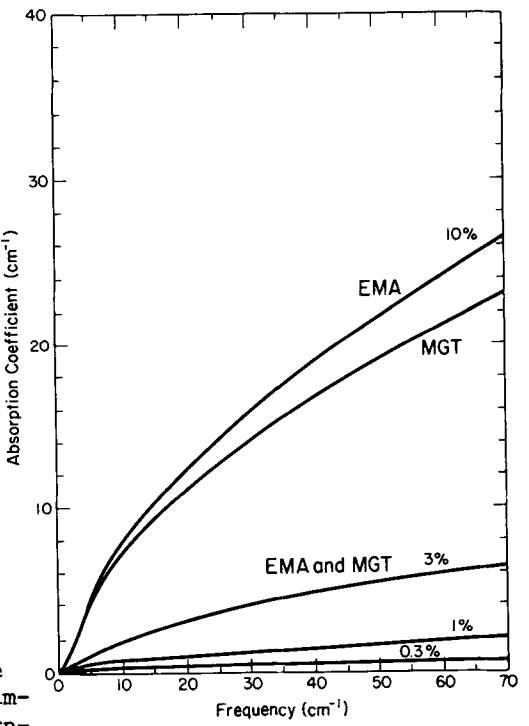

Fig. 3. Calculation for 2 μm Pd particles including eddy currents.

The size dependence of the absorption due to the magnetic dipole effect varies initially as d^2. For the smaller aluminum particles the calculated absorption coefficients are smaller than experiment by

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two orders of magnitude. For example, for d = 500 Å aluminum particles we obtain $\alpha \simeq 70$ f at $\omega = 70$ cm^{-1}.

CONCENTRATION DEPENDENCE

For any batch of particles we observe an increase in absorption coefficient with increasing particle concentration. Figure 4 shows the values of the measured absorption coefficient in the Pd particles at several frequencies, normalized by the value of the absorption coefficient at that frequency for f = 0.01. The absorption coefficient is linear in concentration for f $\lesssim$ 0.03 but rises rapidly for f $\simeq$ 0.1. The predictions of the MGT and EMA are also shown. The MGT predicts a linear concentration dependence for f << 1 (no metal-insulator transition) while the EMA gives a metal-insulator transition at f = 1/3 where α would be very large indeed. The increasing absorption at f $\simeq$ 0.1 is due to the onset of the metal-insulator transition which in these metal-KCl samples occurs in the range 0.15 < f < 0.25.

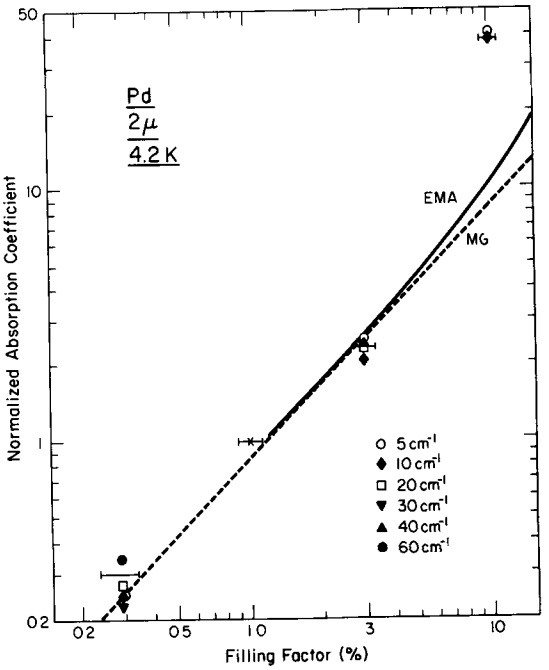

Fig. 4. Normalized absorption coefficient versus concentration.

CONCLUSIONS

We conclude that the magnetic dipole absorption is sufficient to explain the far infrared absorption in relatively large (d $\simeq$ 2 μm) small particles but is unable to account for absorption in smaller particles. Possible explanations include surface layers such as oxide coats,[12] quantum effects[13] or accumulation of many small particles into a macroparticle.

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