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FAR-INFRARED ABSORPTION BY SMALL PARTICLES

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Detailed far-infrared (FIR) and mid-infrared (MIR) studies of aluminum small particles have been carried out. MIR absorption studies of clustered and non-clustered samples suggest that the anomalous FIR absorption does not arise from the clustering together of the individual metallic particles. The MIR absorption, which is too small to be the continuation of the anomalous FIR absorption, could be fitted to the classical theory by using an unexpectedly short electronic mean free path. Evidence is presented for the particles having a non-Drude dielectric function, suggesting that the anomalous FIR absorption is due to the fact that the small particles are not metals.

The far-infrared absorption by small particles has a long history, going back more than forty years [1]. The anomalously large magnitude of the absorption, even in supposedly well-isolated particles, has been investigated for a rather long time also [2]. In this paper we describe infrared studies of Al small particles, comparing the absorption of isolated and clustered particles.

The particles were made by the gas-evaporation technique [3], in which Al metal was evaporated in a He or Ar gas atmosphere at 1–10 torr pressure. This produced a "smoke" powder, consisting of small Al metal particles, approximately 100 Å in size, as determined by electron microscopy. Comparison of bright-field and dark-field images showed that the individual particles had an oxide coating of 10–15 Å thickness. By maintaining a constant pressure of flowing gas and a uniform rate of evaporation, narrow size distributions could be prepared: typical batches had geometric standard deviations [3] of 1.4. The metal smoke was mixed with finely ground powder of KCl or paraffin and compressed into a wafer-shaped pellet for infrared transmission measurements. Metal volume fractions (in the 0.001 to 0.03 range) were estimated from the weights of the constituents, assuming bulk densities.

The extent to which individual metal particles were isolated from one another in these composite samples was determined by the way in which the metal and insulator powders were mixed. To produce well-isolated samples we used a Spex Freezer/Mill to grind the insulator at 77 K, mixed the metal

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powder into the insulator with the aid of the Freezer/Mill, compressed into a pellet, and then reground and recompressed the pellet 4 to 6 times. Less well isolated samples were produced with fewer regrinding steps while the most strongly clustered samples were made with only a single hand grinding in mortar and pestle. In all cases, prior to each compression the Al/KCl samples were baked under vacuum at 150°C to reduce moisture content.

Electron micrographs of a sample which was well mixed are shown in fig. 1a; micrographs of one which was highly clustered are shown in fig. 1b. These

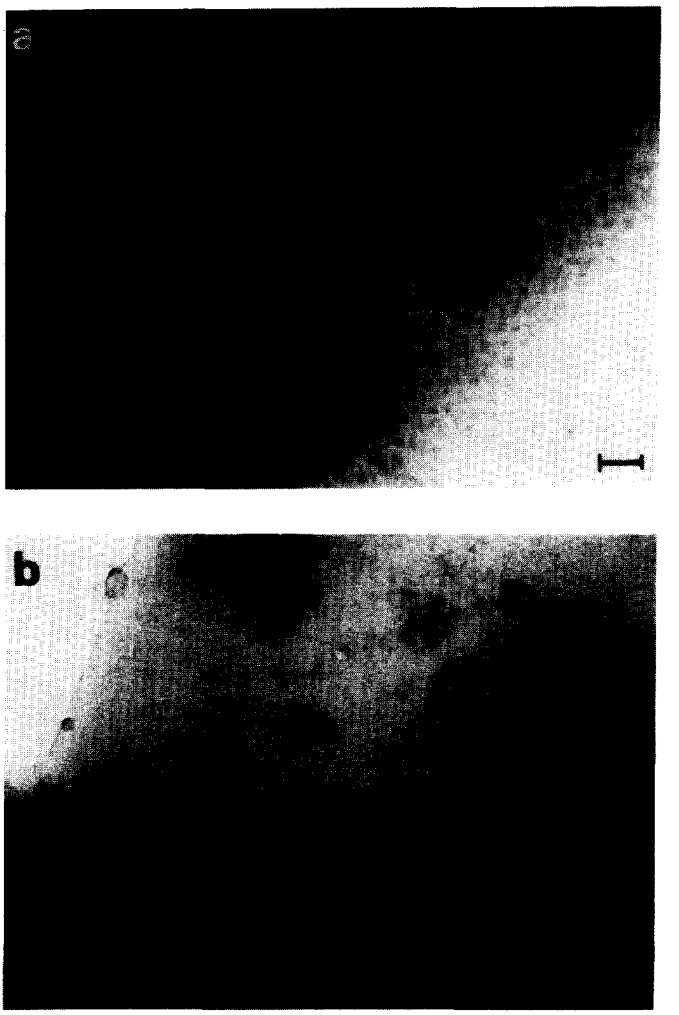

Fig. 1. Electron micrographs of (a) isolated and (b) clustered composite samples. The bars denote 1000 Å.

pictures were made by drilling a hole through a thinned-down sample with an ion mill and then examining the very thin area around the hole with an STEM. Individual isolated particles may be seen as the darkest spots in fig. 1a whereas several particles clumped together are seen in fig. 1b. This clumping was even more evident in lower magnification views.

Fig. 2 shows the far-infrared absorption coefficient of these samples. As in most other measurements [4–7], the data follow

$$\alpha = K_{\mathrm{exp}} f \nu^2 , \tag{1}$$

where f is the metal volume fraction, ν the far-infrared frequency in cm^{-1}, and K_{exp} is the prefactor describing the strength of the absorption. Fig. 2 also shows calculations based on classical theory for Drude-metal small particles [7]. In this theory, the absorption is represented as

$$\alpha = (K_{\mathrm{e}} + K_{\mathrm{m}}) f \nu^2 . \tag{2}$$

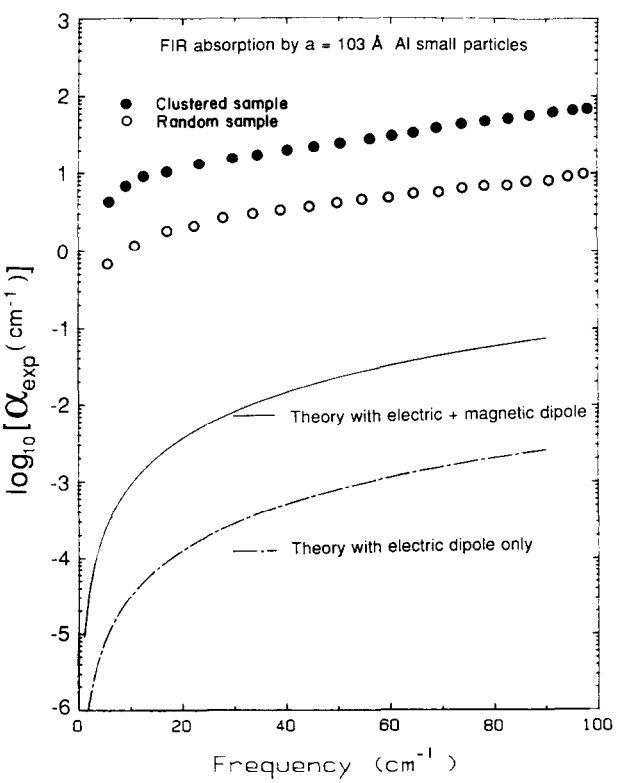

Fig. 2. Far-infrared absorption coefficient of Al/KCl samples with $f = 0.01$.

The coefficients which describe the strength of the absorption, K_e (electric dipole) and K_m (magnetic dipole) are given by

$$K_e = 9\pi c \frac{\epsilon_i^{3/2}}{\sigma_1(1+\sigma_2^2/\sigma_1^2)} \tag{3}$$

and

$$K_m = \frac{8\pi^3 a^2}{5c} \epsilon_i^{1/2} \sigma_1 , \tag{4}$$

where a is the particle radius, σ_1 and σ_2 the real and imaginary parts of the particle's conductivity, and ϵ_i the dielectric function of the material surrounding the particle. Note that both σ_1 and ϵ_i enter with different exponents in eqs. (3) and (4).

The calculated absorption is 100–1000 times smaller than measured; this is the so-called "anomalous" far-infrared absorption [2, 8]. In several recent studies, this anomaly has been attributed to clustering of particles [9, 10, 5]. However, we find an enhanced absorption even in our samples which do not show clustering in the electron microscope studies. Our observation of a further sevenfold enhancement in absorption in the samples which were deliberately made with clustered particles is consistent with the results of Devaty and Sievers [9] and Lee et al. [5].

When the absorption is measured at higher frequencies, three interesting results emerge, illustrated in fig. 3. First, a strong peak is seen at 900 cm^{-1}, with a shoulder at 600 cm^{-1}. The strength and location of this peak is roughly in accord with the data of Ericksson et al. [11], for amorphous aluminum oxide. However, the high absorption at frequencies below 300 cm^{-1} cannot be assigned to the oxide [12]. Second, although the quadratic frequency dependence of eq. (1) continues (as well as the linear volume-fraction dependence), the prefactor is substantially smaller. In the far-infrared (FIR), we find $K_{exp}(\text{FIR}) \sim 0.1$ cm whereas in the mid-infrared (MIR) $K_{exp}(\text{MIR}) \sim 0.001$ cm.

Third, the wide-frequency-range measurements show that the absorption is most likely due to the electric dipole term and *not* the magnetic dipole term of eq. (2). The data in fig. 3 were taken with three different host dielectric constants, ϵ_i: KCl in the far-infrared, where $\epsilon_i = 4.85$, KCl in the mid-infrared, where $\epsilon_i = 2.2$, and paraffin, where $\epsilon_i = 2.1$. Thus, in the top panel, the far-infrared absorption of $f = 0.004$ Al in KCl is substantially larger than the far-infrared absorption of $f = 0.004$ Al in paraffin on account of the higher outside dielectric constant. The lower panel shows that when scaled by $\epsilon_i^{3/2}$ (i.e., normalized to vacuum), the absorption is independent of host. (This does

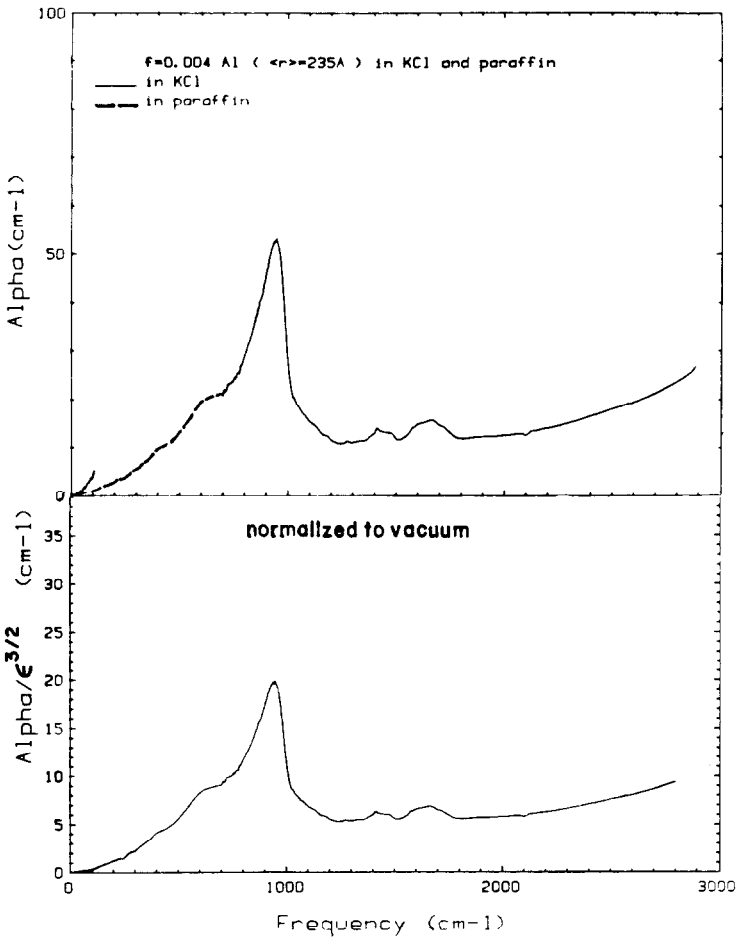

Fig. 3. Far and mid-infrared absorption coefficient of Al/KCl and Al/paraffin samples. Upper panel shows the absorption coefficient; lower panel shows the absorption coefficient scaled by $\epsilon_i^{3/2}$.

not work if the data are scaled by $\epsilon_i^{1/2}$.) The proportionality to the 3/2 power implies that the absorption is due to electric dipole absorption, rather than to magnetic dipole absorption. Indeed, we can fit our mid-infrared data with the electric dipole term of eq. (2), although only by using a rather short (~1 Å) value for the mean free path. (Note that the far infrared absorption by superconducting Sn particles [13] is also consistent with electric dipole absorption [7].)

Given that the absorption is electric dipole, we can invert the absorption coefficient to determine the conductivity of the small particles. The result of such an inversion is shown in fig. 4. In calculating the small-particle conductivity, we have first corrected for reflection losses, the absorption of the host (as

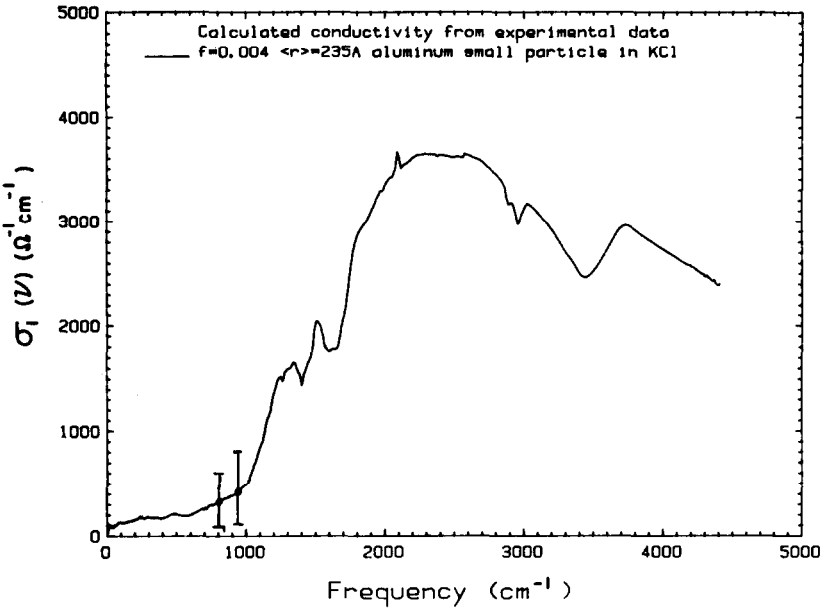

Fig. 4. Frequency dependence of the conductivity of a small metal particle, as inferred from the electric-dipole absorption.

measured) and the absorption of the oxide coating [11]. What is left is presumably due to the metal particles.

This analysis suggests that the classical view that a 100 Å small particle should be treated as a "small Drude metal", may be incorrect. Fig. 4 shows that the far-infrared conductivity of the small particles is extremely small, of order $100\,\Omega^{-1}\,\mathrm{cm}^{-1}$. It then rises to around $4000\,\Omega^{-1}\,\mathrm{cm}^{-1}$, in the mid-infrared. The very low far-infrared conductivity is the reason that the absorption (which goes as $1/\sigma_1$ for the electric dipole term) is so large.

We speculate that the small value of the conductivity is due to quantum size effects. Similar conclusions have been drawn recently by Marquardt et al. [14] in studies of the microwave properties of In small particles, where a very small low frequency conductivity is also found. The electrons within the grain are confined by the particle surface, causing the continuous energy spectrum of the bulk metal to become a series of levels and giving an insulating or semiconductive low-frequency behavior. Only at very high frequencies is the metallic response regained.

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