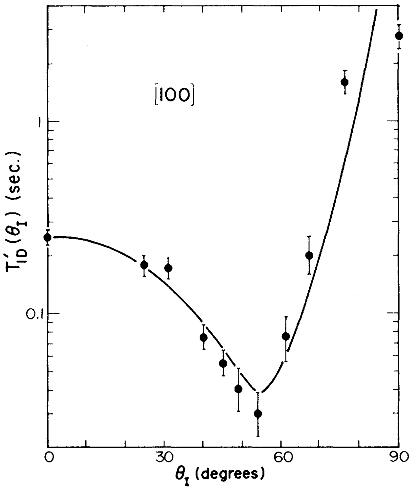

FIG. 3. $T_{1D}'(\theta_I)$ in KF at 200°C. Solid line is calculated from Eq. (5) with one adjustable parameter, $T_{1D}'(\theta_I=0)$.

If I-spin diffusion were dominant, $T_{1D}'(\theta_I)$ would be fairly independent of θ_I except near θ_m, in contrast to our observation.

This technique promises to be a powerful tool for identifying sources and parameters of diffusion of different species in multispin systems. Furthermore, the technique may enable us to study motions which otherwise may be masked by competing processes. In particular, the effect of motions of weakly magnetic and/or dilute spins may be enhanced[2] by this technique. A full account of the theory, an evaluation of $T_{1D}'(\theta_I)$ under various conditions, and more experimental data will be published in a separate paper.

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Far-Infrared Absorption in Ultrafine Al Particles*

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It is shown that the strong far-infrared absorption in small Al particles, recently observed by Granqvist *et al.*, may be explained as arising from the dielectric losses in the amorphous oxide layers covering the particles. Aggregation of particles into clusters is found essential in order to produce the observed dependence of absorptivity on particle size. The propsed mechanism provides a simple understanding of the absence of any superconducting ordering effects in the absorption.

In a recent Letter,[1] Granqvist *et al.* reported interesting results on the far-infrared absorption in powders of small Al particles. For average particle diameter less than 15 nm they find absorptivity which is well approximated by $\alpha(\tilde{\nu}) \simeq C_{\exp}\tilde{\nu}^2$ with the inverse wavelength $\tilde{\nu}$ in the region $3<\tilde{\nu}<150\ \mathrm{cm}^{-1}$. To compare their results with theory the authors calculate the effective dielectric response of a collection of spherical metallic particles, starting from the Maxwell-Garnett[2] approach. Using the Gorkov-Eliashberg[3] (GE) results for the particle polarizability, they obtain an absorptivity $\alpha_{\mathrm{GE}} \simeq C_{\mathrm{GE}}\tilde{\nu}^2$, where the coefficient C_{GE} exhibits a striking disagreement with the experiment. First of all, for average particle diameter $\langle x\rangle \simeq 5$ nm, C_{GE} falls three orders of magnitude short of the experimental value. Moreover, contrary to the experiment, C_{GE} decreases with the average diameter $\langle x\rangle$ as $\langle x\rangle^{-1}$. Similar discrepancies follow if classical Drude theory is used for the electric polarizability of aluminum particles with $\langle x\rangle \lesssim 5$ nm. For larger particles, the eddy-current losses,[4] dominating over the electric dipole losses for $\langle x\rangle \gtrsim 5$ nm, give rise to a classical contribution to C_{Drude} proportional to $\langle x\rangle^3$. Hence the observed size dependence of C_{exp} can be explained by classical theory, but the above discrepancy in the magnitude of the absorptivity remains.[1] Another unexpected result was obtained in earlier measurements[4] on Al, Sn, Cu, and Pb particles of a somewhat larger diameter. In particular, the absorption in superconducting Sn and Pb samples was not affected at all by cooling below their transition temperature.

The purpose of this Letter is to suggest a mechanism of absorption which may explain the large value of C_{exp} observed in Ref. 1, while showing no effects of superconducting ordering. First, I note that the particles used in the above far-infrared studies are always covered with a layer of amorphous oxide, which is expected to give rise to a temperature-independent far-infared absorption. In fact, Strom *et al.*[5] find a strong absorption proportional to $\tilde{\nu}^2$ for $0.1<\tilde{\nu}<100\ \mathrm{cm}^{-1}$ for a variety of amorphous materials. This absorption is T independent, being caused by a disorder-induced coupling of the photon to single phonons.[5] Second, I point out that the particles tend to aggregate into tangled chains and clusters as usually seen in electron micrographs.[6,7] This is expected to be a general property of powders because the large attractive van der Waals interaction between the particles. The high density of metallic cores in these aggregates produces an enhancement of absorption via an interfacial polarization effect.[2,8] To incorporate these observations into a feasible calculation of absorptivity, the following simplified model is used. The sample is imagined to consist of a collection of randomly oriented cylinders with linear dimensions much larger than diameters so that the depolarization end effects can be disregarded.[9] Each cylinder contains spherical metallic cores imbedded in an insulator matrix with the electrical properties of the oxide layer. The effective dielectric constant of this mixture ϵ can be calculated in a mean-field approximation from the expression[10]

$$\epsilon = \epsilon_m\left[1+\frac{3\varphi(\epsilon_p-\epsilon_m)}{\epsilon_p+2\epsilon_m-\varphi(\epsilon_p-\epsilon_m)}\right], \tag{1}$$

where ϵ_m and ϵ_p are the complex dielectric functions of the matrix and metal, respectively. The parameter φ is the volume fraction of the metallic cores in the cylinder. For simplicity, I assume that φ has a fixed value for each cylinder. In the far-infrared region, $|\epsilon_p| \gg |\epsilon_m|$ and the expression (1) reduces to

$$\epsilon = \epsilon_m R, \tag{2}$$

where

$$R = (1+2\varphi)/(1-\varphi). \tag{3}$$

The factor R represents the above-mentioned interfacial enhancement due to metallic cores. It increases with the volume fraction of the metallic phase φ. Denoting by θ the angle between the external field $\vec{E}_0$ and the axis of a cylinder, the dipole moment induced in the direction of $\vec{E}_0$ is given by

$$p_E = \Omega\chi E_0[\cos^2\theta + \sin^2\theta(1+2\pi\chi)^{-1}], \tag{4}$$

where $\chi = (\epsilon - 1)/4\pi$ and Ω is the volume of the cylinder. The average susceptibility $\bar{\chi}$ of a sample containing an isotropic distribution of such cylinders follows from Eq. (4) by angular integration, giving the absorptivity

$$\begin{aligned}\alpha(\omega) &= 4\pi(\omega/c)\,\mathrm{Im}\bar{\chi}\\ &= (\omega/3c)f^*\,\mathrm{Im}\epsilon[1+8(\mathrm{Re}\epsilon+1)^{-2}],\end{aligned} \tag{5}$$

where f^* is the filling factor defined in terms of the total sample volume (including the oxide layer). In the derivation of Eq. (5) the interactions between cylinders are neglected, which is a valid approximation for the small values of f^* used in the far-infrared experiments.[1,4]

Since $\epsilon_m(\omega)$ of the amorphous oxide layers is not known, the numerical estimates of $\alpha(\omega)$ can be made only within an order of magnitude accuracy. Anodic oxide films on Al show[10] a static dielectric constant 8–10, hence I take $\mathrm{Re}\epsilon_m(\omega) \simeq \mathrm{Re}\epsilon_m(0) = 10$. The dielectric losses of amorphous $\mathrm{Al_2O_3}$ have been studied[12] in the radio-frequency region and found to be about 10 times the losses of amorphous SiO_2. I assume the same ratio to hold in the far infrared, where the absorptivity of amorphous SiO_2 has been determined.[5] In this way I estimate for the oxide layer on Al particles $\mathrm{Im}\epsilon_m(\omega) = a\omega$, where a is independent of temperature and equal to 2×10^{-14} sec. Introducing the above estimates in Eq. (5) I obtain finally

$$\alpha(\tilde{\nu}) = 4\times 10^{-3} f^* R \tilde{\nu}^2. \qquad (6)$$

The thickness t of the Al oxide layer is found to be about 1 nm, regardless of the particle size.[6] Assuming that the clusters consist of identical particles with metal core diameter $\langle x\rangle$ arranged on a simple cubic lattice, the metal fraction is calculated to be $\varphi = \frac{1}{6}\pi(1+2t/\langle x\rangle)^{-3}$, a quantity which increases with $\langle x\rangle$. Accordingly, the factor R and also the relative absorption α/f^* increases with the particle size in qualitative agreement with experiment.[1,4] It should be emphasized, however, that only samples with aggregated particles exhibit such a property. For well-separated particles the absorption due to oxide layers would decrease with $\langle x\rangle$. For $\langle x\rangle = 5$ nm, one obtains $\varphi \simeq 0.2$ and $R - 1.7$. The filling factor f^* can be expressed in terms of the metal filling f using relation $f^* = (1+2t/\langle x\rangle)^3 f$. With the value of $f = 1.5\times 10^{-2}$, appropriate for the measurement of Ref. 1, this gives $f^* = 4\times 10^{-2}$. Introducing these values in Eq. (6), I find an absorptivity $\alpha(\tilde{\nu}) = C\tilde{\nu}^2$, where $C \simeq 5.4\times 10^{-4}$ cm. The latter coefficient should be compared with the experimental value[1] $C_{\mathrm{exp}} = 9\times 10^{-4}$ cm. Thus C is three orders of magnitude larger than C_{GE} and C_{Drude} so that it is plausible that the absorption caused by electron excitations of metal cores of Al particles is masked by the dielectric losses in the oxide layers. In particular, the absorption in Al samples is not expected to show any effect due to cooling below its superconducting transition temperature. Qualitatively the same explanation can be offered for Sn and Pb samples for which the absence of an energy gap structure in the absorptivity has already been demonstrated experimentally.[4]

It should be mentioned that the above theory can be checked experimentally by changing the oxide-layer thickness t using different degrees of oxidation during evaporation. The dependence of the absorptivity on t is expected to be particularly simple for samples with well separated particles, thus eliminating the interfacial polarization effect. Yee and Knight[13] have elaborated a technique for preparation of such samples on Mylar substrates for their NMR studies in copper. It is possible that a similar technique could be used with substrates transparent in the far infrared.

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