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Brief Reports

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Far-infrared absorption of small-palladium-particle composites

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We use the recently derived size-distribution-dependent expression for the effective dielectric constant of a composite medium. Because of observed clustering of Pd particles we assume a broad size distribution for the small Pd particles embedded in KCl matrix. We obtain very good agreement between our theoretical calculation and experimental results. Values given by earlier theoretical calculations were by a factor of 10 below those supported by the measured data.

Anomalous far-infrared absorption by random small-metal-particle composites is a well-known fact. Far-infrared measurements of the absorption of small metal particles embedded in a dielectric matrix lead to absorption coefficients which are several orders of magnitude above theoretical calculations.

Russell, Garland, and Tanner[1] found the absorption coefficient of small Pd particles embedded in KCl matrix to be by about a factor of 10 larger than theoretical result based on electric and magnetic dipole absorptions. Carr *et al.*[2] found that the absorption coefficient of small Al particles is by 1 to 3 orders of magnitude above their theoretical calculations, considering again the electric and magnetic dipole absorption.

To explain the discrepancy between the experimental and theoretical results Tanner, Sievers, and Buhrman[3] proposed the quantization of electron energy levels in small metal particles. However, Granqvist[4] concluded that the energy-level quantization cannot explain observed large absorptions. Simanek[5] proposed formation of long chains of oxide-coated metal particles to enhance the absorption. However, Carr *et al.*[2] concluded that oxide absorption is not the dominant mechanism in small-metal-particle composites. Also the estimate of Russell, Garland, and Tanner[1] using Simanek's model[5] does not lead to agreement between theory and experiment.

From a theoretical point of view it has become clear that the classical formulas of Bruggeman[6] and Maxwell-Garnett[7] for an effective dielectric constant of a composite medium cannot account for observed large absorption. Stroud and Pan[8] showed that the theoretically calculated far-infrared absorption is enhanced if one considers magnetic dipole absorption, which is neglected in the formulas of Bruggeman, Maxwell-Garnett, and in most other existing mixing rules. Chýlek and Srivastava[9] derived general expressions for an effective dielectric constant of composite medium considering electric and magnetic dipole absorption as well as the size distribution of small metallic particles. They showed that for the same volume fraction of a metallic component, the absorption of small-metal-particle composites can vary by several orders of magnitude depending on the form of the size distribution of the metallic components.

In this Brief Report we show that theoretical calculations by Stroud and Pan[8] of absorption of small-particle composites can be enhanced up to a factor of 100 by changing the width of metallic component size distribution. We also show that the experimental measurements of absorption of far-infrared radiation by small Pd particles[1] randomly embedded in KCl agrees very well with theoretical calculations when the mixing rule derived by Chýlek and Srivastava[9] is

used.

For the case of aggregate structure (generalization of the Bruggeman[6] mixing rule) Chýlek and Srivastava[9] derived the expression for an effective dielectric constant ϵ in the form

$$\sum_j \left[V_j \frac{\epsilon_j - \epsilon}{\epsilon_j + 2\epsilon} + \frac{2\pi}{45} \left(\frac{\omega}{c} \right)^2 (\epsilon_j - \epsilon) \int r^5 n_j(r)\, dr \right] = 0 \ , \tag{1}$$

where the sum over j runs over all components of a composite medium. V_j and ϵ_j are the volume fraction and dielectric constant of the jth component, respectively. Small particles are assumed to be spherical with the radius r and the size distribution $n_j(r)$.

Consider a two-component composite. Let one of the components be a dielectric [the second term in the sum in Eq. (1) can be neglected] with a dielectric constant ϵ_1. If V is the volume fraction, ϵ_2 the dielectric constant, of a metallic component, and

$$n(r) = a r^{\alpha} \exp(-\alpha r / r_m) \tag{2}$$

the size distribution (a and α are positive constants, r_m is a mode radius), Eq. (1) reduces into[9]

$$(1-V)\frac{\epsilon_1 - \epsilon}{\epsilon_1 + 2\epsilon} + V\frac{\epsilon_2 - \epsilon}{\epsilon_2 + 2\epsilon} + V\frac{1}{30}\left(\frac{\omega r_m}{c} \right)^2 \frac{\Gamma(\alpha+6)}{\alpha^2 \Gamma(\alpha+4)} (\epsilon_2 - \epsilon) = 0 \ , \tag{3}$$

which is a cubic equation for the unknown effective dielectric constant ϵ of a composite medium.

To illustrate the effect of a size distribution on the effective dielectric constant of a composite system, we consider a dielectric-metal composite with $\epsilon_1 = 1$ and ϵ_2 given by a Drude dielectric function

$$\epsilon_2 = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau)} \ , \tag{4}$$

where ω_p is the plasma frequency and τ is a relaxation time. For a numerical example we take $V = 0.15$, $\omega_p r_m / c = 1$, $\omega_p \tau = 100$, and we calculate the $\mathrm{Im}[\omega/c(\epsilon)^{1/2}]$ for the range of $10^{-3} < \omega/\omega_p < 10^{-1}$. The results are shown in Fig. 1. The case of $\alpha = 1000$ corresponds to a very narrow (about a δ function) size distribution. In this case our results are identical with those of Stroud and Pan.[8] However, by taking $\alpha = 10$ (narrow size distribution), $\alpha = 1$, and $\alpha = 0.5$ (broad size distribution) and keeping the mode radius r_m and the volume fraction V of a metallic component unchanged, the absorption coefficient can be enhanced by up to a factor of 100.

For the case of Pd particles randomly embedded in KCl we use $\epsilon_1 = 4.8$ for KCl and a Drude-type dielectric constant (4) for palladium with $\omega_p = 5 \times 10^4\ \mathrm{cm}^{-1}$ and $\tau\omega_p = 100$. We took $r_m = 1\ \mu$m in agreement with the size of Pd particles used in the experimental arrangement of Russell, Garland , and Tanner.[1] Since the clustering of particles was observed[1] with the typical size clusters of about 5 μm, we assume a wide size distribution with $\alpha = 0.5$.

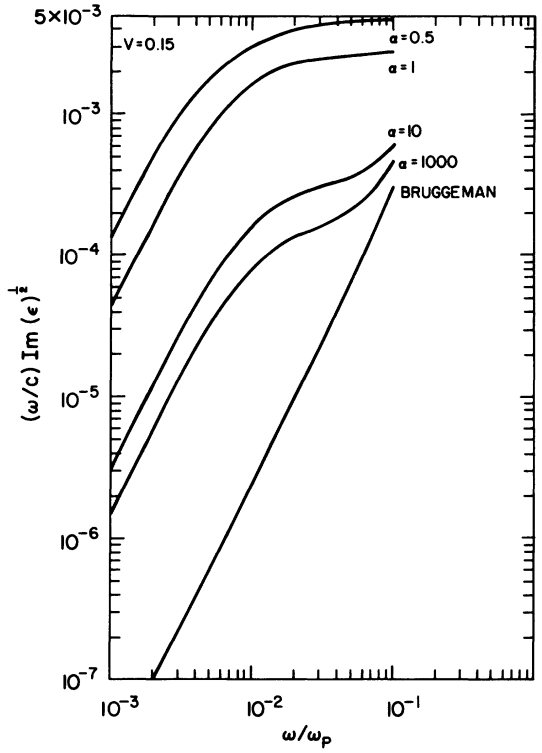

FIG. 1. The absorption following from the use of the Bruggeman mixing rule is enhanced by more than a factor of 10 by including magnetic dipole interaction assuming the δ-function ($\alpha = 1000$) size distribution for Pd particles. The absorption can be increased by another factor of 100 assuming a broad size distribution ($\alpha = 0.5$ is comparable to log-normal distribution with $\sigma_g = 2.5$). Numerical calculations are for $V = 0.15$ and $\omega_p r_m / c = 1$.

Comparison of our calculation with the experimental measurements of Russell, Garland, and Tanner[1] is shown in Fig. 2. As can be seen we obtain a good agreement in most cases.

Agreement is quite good at the volume fractions $V = 0.001$, 0.003, and 0.01. Disagreement at $V = 0.1$ may be caused by enhanced clustering of Pd particles at high concentrations leading possibly to a higher value of the mode radius of the size distributions. If clustering occurs it is natural to expect the size of clusters to grow with increasing concentration. Our results indicate, that below the volume fraction of $V \leq 0.03$ the size of clusters is independent of the

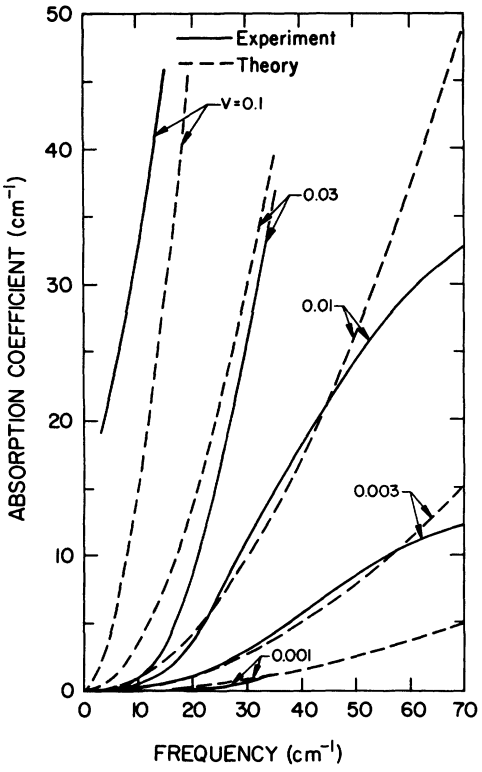

FIG. 2. Good agreement between the measured and calculated absorption coefficient $2(\omega/c)\,\mathrm{Im}(\epsilon)^{1/2}$ is obtained assuming a wide size distribution of Pd particles with $\alpha=0.5$. The mode radius $r_m=1$ μm is in agreement with the particles used in the experiments.

volume fractions. However, the size of clusters appearing at $V=0.1$ is considerably larger. At volume fraction $V=0.030$ our calculations systematically overestimate the measured absorption coefficient. However, if instead of $V=0.030$ we use $V=0.026$, we obtain again a good agreement between theory and experiment. Theory predicts a quadratic dependence of absorption coefficient on ω. It does not show the saturation observed experimentally at lower values of the volume fraction ($V=0.003$ and $V=0.01$).

By using the size-distribution-dependent expression for the effective dielectric constant of a composite medium,[9] the effective dielectric constant of a composite system can be enhanced by several orders of magnitude.

In the case of small palladium particle composites good agreement between theory and experiment[1] is obtained under the assumption that clusters of several particles are formed within a composite system. The result of clustering is considerably wide size distribution of metallic particles.

Since clustering to the size of 5 μm was observed during the experiment,[1] we consider the presence of a wide size distribution to be an acceptable explanation of the high measured absorption.

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