Effect of Melting of the Metallic Component on the Anomalous Far-Infrared Absorption of Superconducting Sn Particle Composites

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By means of a simple experimental heat-treatment procedure, the anomalous far-infrared absorption of superconducting Sn particle composites is shown to be associated with clustering. The structural insights thus obtained lead to a new theory in which the composite electric dipole absorption is dominated by poorly conducting clusters and is much larger than that of isolated metal particles. For superconducting particles, the theory predicts the absorption at frequencies above the gap frequency to be larger than in the normal state, in agreement with experiment.

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Recent experiments by Carr, Garland, and Tanner[1] on granular superconducting samples of small Sn particles embedded in an insulating alkali halide host have shown that not only is the absorption anomalously large in comparison to the predictions of classical theories,[2,3] but at frequencies higher than the superconducting gap frequency ω_g the composites are actually more absorbing in the superconducting state than in the normal state. Though carried out on a different class of system, the experimental work of Devaty and Sievers suggests that in the normal state this large absorption is a multiparticle effect.[4] The superconducting behavior is surprising since bulk Sn has smaller electromagnetic absorption in the superconducting state.

In this paper we (i) report far-infrared absorption measurements for composite samples comprised of either oxide-coated or oxide-free Sn particles in KBr at low temperatures, and (ii) present a new theory that accounts for the absorption in these systems. With respect to the measurements, we have found that both types of system show greater absorption in the superconducting state than in the normal state at frequencies higher than ω_{gap}. However, as we shall see below, after heat treatment, a process presumed to change the local particle topology, the absorption in the superconducting state is found *never* to exceed that of the normal state. The structural implications of these results suggest a new theoretical description of such systems. In particular, the unheated-sample results may now be understood by the assumption that the absorption is attributable to clusters of metal particles with effective dielectric properties which depend on the local particle topology. One particular cluster topology (the cluster percolation model) is most likely to be appropriate for the unheated composites. It is characterized by poorly conducting clusters (as compared to that of the metal particle constituents) and leads to large electric dipole (ED) absorption because of the dependence of the absorption on the inverse of the cluster conductivity in the ED mechanism. The superconducting anomaly then arises quite naturally for the ED absorption mechanism.

The Sn particles used in this study are produced by a method of inert-gas evaporation.[5] Sn metal is evaporated from a molybdenum boat in either a 20% oxygen: 80% argon or a 100% argon atmosphere at a pressure of 0.7 Torr. The particles prepared in the presence of the oxygen have a thin oxide coating which prevents them from cold welding together during the evaporation process. These samples are chosen to be similar to those studied by Carr, Garland, and Tanner. Particles made in a pure argon atmosphere are assumed to have no oxide coating. A scanning transmission electron microscope is used to measure the particle sizes: The oxide-coated and oxide-free particles discussed here have mean radii of 50 Å (including the oxide coating of[1] ≤ 20 Å) and 250 Å, respectively. Our samples are pressed pellets[1] of Sn particles embedded in a KBr host. The metal volume fill fraction is 0.02. Because of continuous radiation damage to the alkali halide as well as sample thinning problems, neither we nor others before us have been able to make direct TEM studies of the sample morphology.

Several of the composite samples were subjected to the heat treatment process mentioned above. This consists of heating the finished pellets for 15 min at a temperature of 250°C, which *exceeds* the bulk Sn melting point of 232 °C but is still well below the melting point of KBr. Either air or hydrogen atmosphere is used in heat treating of the oxide-free samples. Hydrogen is used to inhibit the formation of an oxide coating. Identical absorption coefficients are obtained for these different atmospheres. An air atmosphere is used exclusively in heat treating of the oxide samples. The Sn particles from the heat-treated samples were later examined with a TEM after removal of the alkali halide host with water. The micrographs show numerous large Sn single crystals with mean radii of 500 and 800 Å embedded in relatively large structureless 2000–3000 Å Sn clusters for the heated oxide and oxide-free samples, respectively.

Transmission spectra were measured from 4 to 30 cm^{-1} with a lamellar grating interferometer and a cryostat with a ^{3}He-cooled germanium bolometer.[4] The infrared absorption coefficient is then calculated from the measured transmission coefficient $T(\omega)$ by

$$\alpha(\omega) = (1/t)\ln T(\omega) + \alpha_0,$$

where t is the thickness of the sample and α_0 is chosen so that the absorption coefficient extrapolates to 0 at zero frequency.

The normal-state absorption coefficient for representative unheated and heated oxide-coated and oxide-free samples is shown in Fig. 1. In complete agreement with previous studies of FIR absorption by small particles in alkali-halide hosts, the magnitude of α_n is orders of magnitude larger than predicted by simple theories. Here, both types of unheated samples show nearly quadratic frequency dependence at low frequencies but the oxide-coated sample data becomes nearly linear in frequency above 15 cm^{-1}. Upon heat treatment, the normal-state absorption of the oxide samples changes only slightly. However, the absorption of the oxide-free samples decreases by about a factor of 2 in magnitude and the frequency dependence is between linear and quadratic.

The superconducting-state results are also interesting: Distinct changes in the difference absorption $\Delta\alpha = \alpha_n - \alpha_s$ appear for both sample types upon heat treatment as shown in Fig. 2. Before heating, both sample types exhibit a superconducting absorption which is larger than the normal-state absorption above $\omega_g = 9.3$ cm^{-1}, as also reported by Carr, Garland, and Tanner. At frequencies below ω_g, $\Delta\alpha$ for the oxide-coated samples is small and its sign varies from sample to sample. But, for the oxide-free samples $\Delta\alpha$ is definitely positive. After heat treatment, the oxide-coated samples give $\Delta\alpha \approx 0$ over all of the frequency range studied. In contrast, $\Delta\alpha$ for the oxide-free samples becomes positive at all measured frequencies.

The changes in both α_n and $\Delta\alpha$ induced by the heat treatment are taken as strong evidence that clustering is indeed responsible for the anomalous FIR absorption in these systems. Our observations of large fused clusters present in the heat-treated samples suggest a general picture of the composite topology in which compact clusters of metal particles with effective local dielectric functions ϵ are distributed evenly throughout the host medium. We now describe the theory of one such cluster topology (the cluster percolation model), appropriate to the *unheated* samples, which predicts very large electric dipole absorption.

In the cluster percolation model, the composite is assumed to consist of dispersed clusters, on a size scale of a few thousand angstroms, embedded in the alkali halide host. Each cluster is itself a subcomposite consisting of metal particles of radius a, voids, and impurities and/or oxides. The latter serve to electrically isolate a fraction $1-p$ of the metal particles from their neighbors. The remaining metal particles in the cluster are taken to be electrically coupled

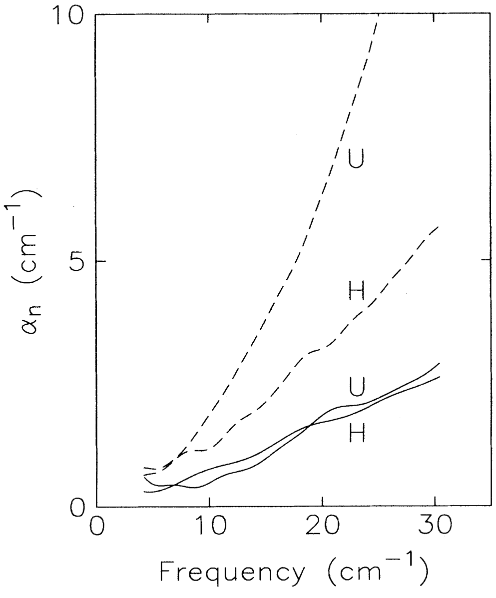

FIG. 1. Normal-state absorption coefficient α_n for oxide-coated (solid lines) and oxide-free (dashed lines) samples before (U) and after (H) the heat-treatment process. All the α_n are anomalously large with respect to previous theoretical predictions. The uncertainties in the measured α are ±5%.

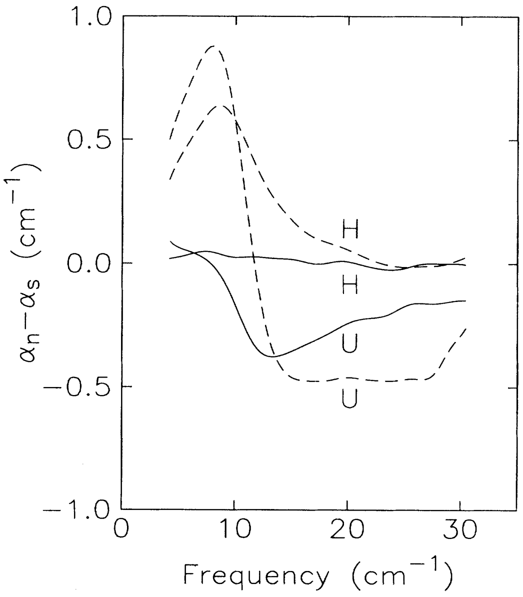

FIG. 2. Difference absorption $\Delta\alpha = \alpha_n - \alpha_s$ for oxide-coated (solid lines) and oxide-free (dashed lines) samples before (U) and after (H) heat-treatment process. Note the disappearance of the $\Delta\alpha(\omega > \omega_g) < 0$ anomaly seen by Carr, Garland, and Tanner upon heat treatment.

to an extent appropriate for a finite-sized system of metal particles of fill fraction p and complex dielectric $\epsilon_m(\omega)$ embedded in a nonconducting cluster host with dielectric ϵ_b. The cluster is characterized by an effective dielectric function $\epsilon(p,\omega)=\epsilon'(p,\omega)+i\epsilon''(p,\omega)$. The composite is an assembly of clusters with a range of p values. Clusters with p near 1 are very metallic and have small electric dipole absorption. Clusters with p near 0 consist of isolated metal particles and their absorption is again small, being similar to that of a system of small isolated particles. However, for clusters with p near the threshold for percolation, p_c, the electrically coupled metal particles will form tenuous chains and the absorption of such clusters is greatly enhanced relative to single particles.

The clusters with their associated $\epsilon(p,\omega)$ are assumed to be uniform in size and much smaller than the wavelength of the incident radiation. In addition, since the total metal fill fraction is $f << 1$, the fill fraction of each "bin" of clusters, $fN(p)dp$, where $N(p)$ is the fraction of clusters with conducting-element fill fraction between p and $p+dp$, is also necessarily small. Within these limits, the multicomponent Maxwell-Garnett[3,6] dielectric function for a dilute collection of spherical inclusions is then applicable, and leads to

$$\epsilon_{\mathrm{comp}}(\omega)=\epsilon_h\left\{1+3f\int dp\, N(p)\frac{\epsilon(p,\omega)-\epsilon_h}{\epsilon(p,\omega)+2\epsilon_h}\right\}, \quad (1)$$

where ϵ_h is the KBr host dielectric constant. The absorption coefficient arising from electric dipole absorption is $\alpha(\omega)=2(\omega/c)\mathrm{Im}\,\epsilon_{\mathrm{comp}}^{1/2}$ and is approximately given by

$$\alpha(\omega)\approx 9f\epsilon_h^{3/2}\frac{\omega}{c}\int dpN(p)\frac{\epsilon''(p,\omega)}{\epsilon'(p,\omega)^2+\epsilon''(p,\omega)^2}. \quad (2)$$

Large absorption results if there exist clusters with $\epsilon'\approx\epsilon'' << \epsilon_m''$, a condition we will show to be generally satisfied. The distribution function $N(p)$ is not in general explicitly known. However, we expect $N(p)$ to be relatively featureless over the scale of the substantial variations in the dielectric function anticipated at $p\approx p_c$. By way of example, we have chosen $N(p)$ to be a constant over $0<p<0.30$ and zero elsewhere, a choice which provides merely an overall scale factor for the absorption.

To calculate the effective dielectric function $\epsilon(p,\omega)$ of a single cluster characterized by a chosen p, the structure is geometrically modeled as a simple cubic lattice spacing $2a$ and edge length L. Between the sites of the lattice are placed dielectric bonds assigned a dielectric constant of either $\epsilon_m(\omega)$ or ϵ_b with the fraction of p of $\epsilon_m(\omega)$ bonds corresponding to the volume fraction of unisolated metal particles. The metal dielectric function is assumed describable by a Drude model with an electron relaxation time $\tau=a/v_f$. The cluster host dielectric constant ϵ_b has contributions from the coated metal particles and is taken to be a real constant. An effective $\epsilon(p,\omega)$ may then be calculated in principle for the model cluster by averaging over the many possible configurations of conducting and nonconducting bonds at fixed p. This lengthy procedure can, however, be avoided by employing a real-space renormalization-group (RSRG) technique[7] to calculate $\epsilon(p,\omega)$. For a finite system, the RSRG transformation, which reduces the number of bonds along a cube edge by a factor of 2 after each transformation, is truncated after $\ln(L/2a)/\ln(2)$ iterations so that an $L\times L\times L$ cluster with fraction p of $\epsilon_m(\omega)$ bonds is reduced to a single effective cluster of dielectric $\epsilon(p,\omega)$.

Utilizing this approach, we find that the real part of $\epsilon(p,\omega)$ increases slowly with increasing p; in contrast, the imaginary part increases very rapidly from values much less than the real part to values much greater than the real part, over a fairly narrow ($0.1<p<0.25$) range of p. This transition constitutes the remnant of the insulator-metal transition of infinite clusters and guarantees that the absorption coefficient [see Eq. (2)] will have contributions from clusters with $\epsilon'(p,\omega)=\epsilon''(p,\omega) << \epsilon_m''(\omega)$, as is necessary for large absorption. The frequency dependence of $\alpha(\omega)$ is sensitive to the details of the calculation of $\epsilon(p,\omega)$ but our model results should be a reasonable representation of the actual $\epsilon(p,\omega)$ and the resultant absorption coefficient. We emphasize that the general behavior of $\epsilon(p,\omega)$ and hence α is expected for any type of calculation incorporating the essential physics. The RSRG technique merely puts the transition of $\epsilon(p,\omega)$ from insulating to metallic behavior in a particular range of p with a (size-dependent) width and frequency dependence.

The absorption coefficient versus frequency as calculated by Eq. (1) [with $\epsilon(p,\omega)$ as appropriate for $a=50$ Å Sn particles in clusters of sizes $L=64a=3200$ Å] is presented in Fig. 3. The parameters have been chosen to correspond to the unheated oxide-coated samples studied here with $\epsilon_b=10$. The magnitude of the absorption at low frequencies is fairly large: $\alpha(8\ \mathrm{cm}^{-1})\approx 0.075\ \mathrm{cm}^{-1}$, which is within a factor of 4 of the measured value and exceeds the Maxwell-Garnett single-particle estimates by about 3 orders of magnitude. The frequency depedence is also in good agreement with the data.[8] The magnitude of α is fairly insensitive to the magnitude of $\epsilon_m''(\omega)$ and nearly proportional to $\epsilon_b^{-1/2}$.

For the superconducting state, the composite absorption coefficient may be calculated with the same procedure but with the use of the Mattis-Bardeen[9] dielectric function for the superconducting metallic

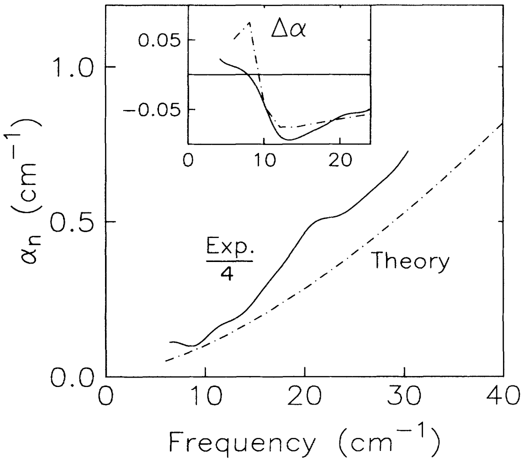

FIG. 3. Normal-state absorption coefficient in cluster percolation model (dot-dashed lines), for clusters of size $L = 3200$ Å, particle diameter $2a = 100$ Å, corresponding to the non-heat-treated oxide-coated samples studied here. Inset: $\Delta\alpha(\mathrm{cm}^{-1}) = \alpha_n - \alpha_s$ vs $\omega(\mathrm{cm}^{-1})$ calculated with the same model with $\omega_g = 8$ cm^{-1}. The measured α_n and $\Delta\alpha$ for unheated oxide samples of Figs. 1 and 2 scaled down by an arbitrary factor of 4 are also shown (solid lines).

component. The difference absorption $\Delta\alpha$, shown in the inset of Fig. 3, exhibits a positive peak near ω_g (taken to be at 8 cm^{-1}) and a negative peak at a higher frequency followed by a decrease in $\Delta\alpha$ to zero at $\omega >> \omega_g$. The calculated $\Delta\alpha$ is quite consistent with experimental observations. The "anomalous" (i.e., $\Delta\alpha < 0$) absorption results directly from the form of Eq. (2). In the superconducting state, ϵ'' is reduced from its normal-state value and ϵ' increased such that the absorption is actually increased relative to that of the normal state for $\omega > \omega_g$.

Upon heat treatment, we expect the metal particles in each cluster to fuse together despite the presence of the coating on some preheated particles. Fusion represents a drastic change in the cluster topology and should consideralby alter the character of the absorption coefficient. In particular, we expect the oxide-free sample clusters to become quite metallic and exhibit large magnetic dipolelike absorption upon heat treatment, yielding $\Delta\alpha > 0$ above ω_g.[10] However, for the oxide-coated samples, the presence of the oxide must prevent a complete transition from the cluster percolation topology to a fused metallic cluster topology and $\alpha(\omega)$ should then result from a combination of the mechanisms just described.

In summary, heat treatment of metal–alkali-halide composites greatly affects their absorption coefficients and eliminates the $\Delta\alpha < 0$ superconducting "anomaly." A cluster percolation model, in which the connectivity within a cluster is sensitive to the melting of the metal component, leads to clusters some of which satisfy a resonance condition $\epsilon' \approx \epsilon''$ in the absorption with ϵ' and ϵ'' much smaller than ϵ''_m. The resulting absorption coefficients are in good agreement with experiment, resolving not only the $\Delta\alpha < 0$ anomaly of Carr, Garland, and Tanner but also the long-standing discrepancy of orders of magnitude difference between theory and experiment in such systems.

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