Anomalous Infrared Absorption in Granular Superconductors

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Granular superconductors are shown to have a far-infrared absorption that is larger when the samples are superconducting than when they are normal. By contrast, theoretical models for these materials predict that when the samples become superconducting, the absorption should decrease.

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The dominant feature in the excitation spectrum of a superconductor is the presence of an energy gap, Δ. There is no energy loss when a superconductor (at $T=0$) is subjected to electromagnetic radiation with frequency less than 2Δ; for dc the conductivity is infinite while at finite frequencies the response is purely inductive. The frequency-dependent conductivity, $\sigma_{1s}(\omega)$, which governs the absorption, is zero for $0<\omega<2\Delta$, becomes finite but small at $\omega=2\Delta$, and rises slowly to meet the normal-state conductivity, σ_{1n}, at two or three times the threshold frequency.[1]

In this Letter we report the observation of an unexpected increase in far-infrared absorption when highly granular materials undergo the transition from normal to superconducting. Our samples, three-dimensional random composites and two-dimensional granular films, behave as expected when $\omega \ll 2\Delta$: The films have zero dc resistance while the composites become less absorbing than when normal. In contrast, when $\omega \sim 2\Delta$, the absorption in the superconducting state exceeds that of the normal state by about 50%. The composite samples also show an anomalously large normal-state absorption, as is typical for small metal particles.[2-4] The two anomalies are closely connected in that the amount of increased absorption in the superconducting state is proportional to the strength of the normal-state absorption. At present, both effects remain unexplained.

Our first type of sample was a composite of small Sn or Pb particles embedded randomly in a KCl host. Small metal particles ("smoke") were made by evaporation in the presence of a noble-gas–oxygen mixture.[5] Typical conditions, which consisted of evaporation at just above the melting point in a 3:1 argon-oxygen mixture at 1 Torr, gave median particle radii of about 200 Å with an expected[5] oxide thickness[6] of 20–40 Å. A small amount of this smoke was mixed with finely divided KCl and compressed into a wafer-shaped sample. The wafer was reground and recompressed several times to homogenize the constituents. The metal volume fraction, f, determined by weighing the constituents, was $0.001 \leqslant f \leqslant 0.05$ (well below the critical volume fraction for conduction of about 0.20).

Our second type of sample was a granular Pb film, prepared by ion-beam sputter deposition. The electrical resistance of the film was monitored during deposition so that the process could be stopped when a desired resistance was reached. Without breaking vacuum, SiO_2 was deposited over the Pb film. This encapsulation procedure was very effective in maintaining the stability of the Pb film with time. The films consisted of irregularly shaped metal islands, typically 1000 to 3000 Å in size, separated by narrow channels. The sheet resistance of the films correlated well with the size and separation of these islands, with high–sheet-resistance films having the smaller and more isolated islands.

The individual grains in our samples appeared to be close to bulk material in their behavior. The heat capacity[7] of Sn small particles (with the same size as the smoke used in our samples) had a slightly smeared jump occurring very near the bulk transition temperature of 3.7 K. The intermediate- and low-sheet-resistance films were superconductors for dc with broadened resistive transitions beginning at about 7.2 K, as expected for Pb. Critical currents were typically a few milliamperes; the I-V characteristics displayed steps and hysteresis, which we take as evidence for Josephson coupling between the grains.

We measured the far-infrared transmission of our samples using a lamellar grating interferometer and a 1-K germanium bolometer. The useful frequency range of this combination (4–50 cm^{-1} or, equivalently, 0.5–6 meV) spanned the energy gaps of Sn (9.3 cm^{-1}) and Pb (22 cm^{-1}). The superconducting-state measurements were done at a temperature of 1.8 K while the normal-state measurements were done at 15 K. No temperature dependence was observed between the transition temperature and 30 K.

The far-infrared absorption coefficient $\alpha(\omega)$ (corrected for reflection loss[8]) for two Sn-KCl composites is shown in Fig. 1. Data are shown for samples with median particle radii of 50 and 150 Å. In all, twenty Sn-KCl and Pb-KCl composites showed results very similar to those illustrated here. The normal-state absorption coefficient, α_n, obeyed[2]

$$\alpha_n = Kf\omega^2, \qquad (1)$$

where the factor K is a measure of absorption strength. The most obvious feature of the superconducting-state absorption coefficient, α_s, is that it exceeds the normal-state absorption over $8 < \omega < 20\ \text{cm}^{-1}$.

The relative changes in absorption between the normal and superconducting states were similar for different samples. Figure 2 shows the normalized differential absorption coefficient, $\Delta\alpha = (\alpha_s - \alpha_n)/Kf$, for two samples. Although the product Kf differs by a factor of 300 among our samples, this normalized differential absorption varies by no more than a factor of 2 with similar particle sizes but with "low" and "high" amounts of oxidation.

Our granular films behave very much like our composite samples. Figure 3 shows the ratio of transmittance in the superconducting state to transmittance in the normal state, T_s/T_n, for three Pb films having different sheet resistances. Each has a minimum in the transmission ratio, i.e., a maximum in the absorption, in the 10- to 20-cm^{-1} region. At higher and lower frequencies the transmission ratio is nearly unity. All of our films with sheet resistance above 50 Ω/□ behave as do those shown in Fig. 3.

In an attempt to explain our measurements, we have employed commonly used models, with the hope that these simple models might give a qualitative understanding of our results. The absorption coefficient of the Sn-KCl composites was calculated from the Maxwell-Garnett effective dielectric function,[4] which in its long-wavelength limit is

$$\alpha = (\epsilon_i)^{1/2} f \frac{\omega^2}{c^2}\left[\frac{9c\epsilon_i\sigma_{1m}}{4\pi(\sigma_{1m}^2 + \sigma_{2m}^2)} + \frac{2\pi a^2\sigma_{1m}}{5c}\right], \qquad (2)$$

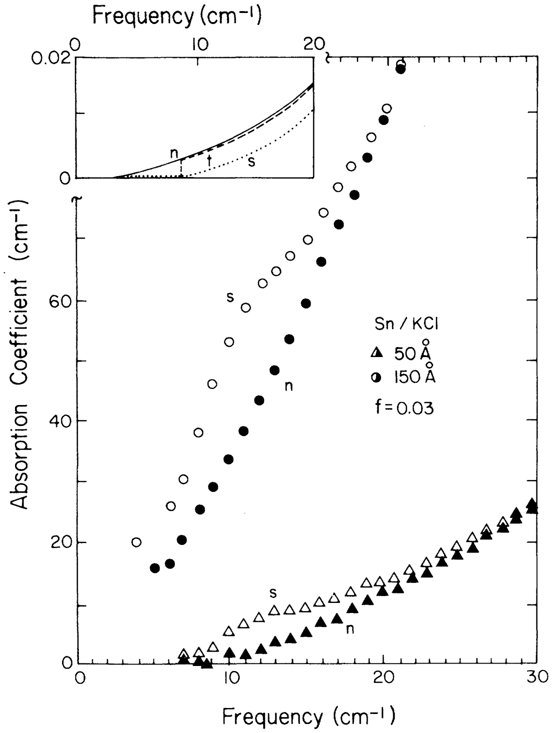

FIG. 1. Far-infrared absorption coefficient of two Sn-KCl composities in the normal state (filled symbols) and the superconducting state (open symbols). Inset (on a changed scale): The result of calculations for the normal state (solid line), the superconducting state (dotted line), and the tunneling model (dashed line).

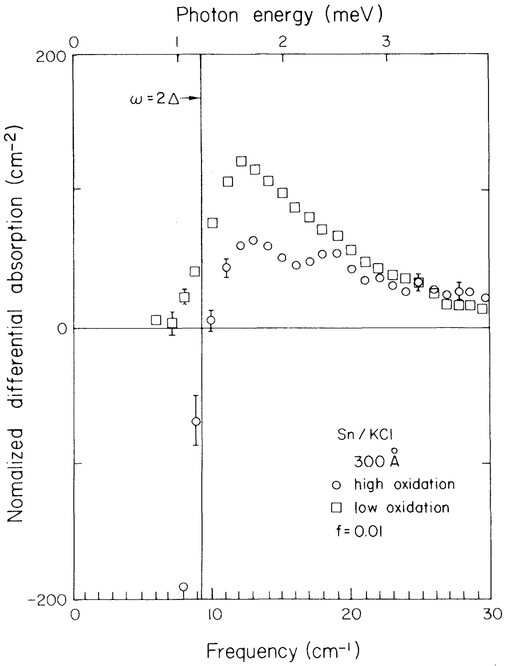

FIG. 2. Difference between superconducting-state and normal-state absorption for two Sn/KCl composites, one with "high" and one with "low" Sn oxidation. The vertical line occurs at the Sn energy gap.

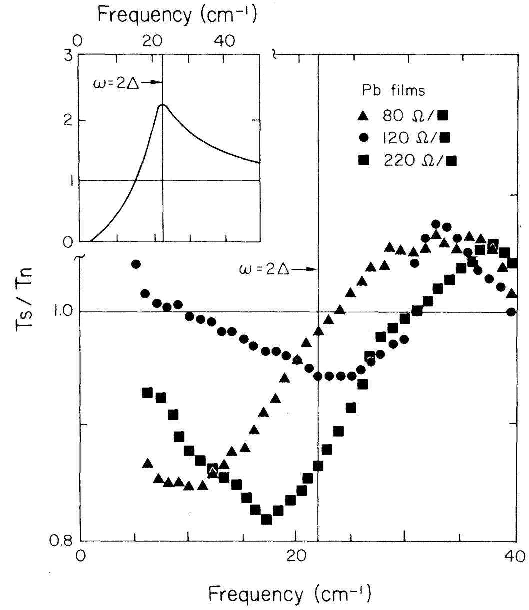

FIG. 3. Ratio of superconducting-state to normal-state transmission for three granular Pb films vs frequency. Inset: Calculated transmission ratio.

where $\epsilon_i = 4.84$ is the KCl dielectric constant, a is the particle radius, and σ_{1m} and σ_{2m} are respectively the real and imaginary parts of the conductivity of the metal particle. In Eq. (2) the first term describes electric dipole absorption and the second describes magnetic dipole (or eddy current) absorption. The second dominates when $a > 50$ Å for metallic values of σ_{1m}. In the normal state $\sigma_{1m} = \sigma_{1n} = 10^6\ \Omega^{-1}\ \mathrm{cm}^{-1}$ and $\sigma_{2m} \approx 0$ while in the superconducting state $\sigma_{1m} = \sigma_{1s}$ and $\sigma_{2m} = \sigma_{2s}$ with σ_{1s} and σ_{2s} obtained from the $T = 0$ Mattis-Bardeen[1] calculations with the assumption of the bulk energy gap. The predictions of this model[9] are shown in the inset in Fig. 1. The normal-state absorption (solid line) is quadratic whereas the superconducting-state absorption (dotted line) is zero for $\omega < 2\Delta$, becomes finite at 2Δ, and increases at higher frequencies; it is always smaller than the normal-state absorption.

Because the data disagree with the simple model of superconducting grains in an insulating host, we considered also the effects of photon-induced tunneling between grains.[10] A tunneling mechanism would be expected to enhance the absorption near the gap (where the BCS density of states has square-root singularities). For $\omega < 2\Delta$, we have $\alpha = 0$, while for $\omega > 2\Delta$, the absorption is

$$\alpha_s/\alpha_n = \omega^{-1} \int_{\Delta}^{\omega - \Delta} N(E) N(\omega - E) dE, \qquad (3)$$

where $N(E) = E/(E^2 - \Delta^2)^{1/2}$ is the density of states. The result of this model is shown as the dashed line in the inset in Fig. 1. The absorption coefficient is zero below 2Δ, jumps almost to the normal-state absorption at $\omega = 2\Delta$, and increases parallel to that absorption at higher frequencies. It never exceeds the normal-state absorption.

The amount of light transmitted through a thin film (thickness d) into a substrate (refractive index n) is given by

$$T = \frac{4n}{[n + 1 + (4\pi/c)\sigma_{1f} d]^2 + [(4\pi/c)\sigma_{2f} d]^2}, \qquad (4)$$

where σ_{1f} and σ_{2f} are respectively the real and imaginary parts of the conductivity of the film. In the normal-state and long-wavelength limit, $\sigma_{2f} = 0$ and σ_{1f} is equal to the dc conductivity, making T_n independent of frequency. In the superconducting state, both real and imaginary parts of the conductivity are important, yielding the transmission ratio T_s/T_n shown as the inset in Fig. 3. This ratio is a maximum at $\omega = 2\Delta$; it falls to zero as $\omega \to 0$; and it goes to unity at high frequencies. Our films with low sheet resistances ($R < 50\ \Omega/\square$) displayed this ordinary behavior although the maximum was often not as high as calculated; in contrast, the films with $R > 50\ \Omega/\square$ behaved like those in Fig. 3.

We are unable to advance an explanation for our observation of enhanced far-infrared absorption in granular superconductors. That this effect is related closely to the anomalous normal-state absorption[2-4] by small metal particles seems very likely. Photon-induced tunneling between adjacent grains is unable to explain the effect, just as classical models of interacting clusters of particles were unable to explain the normal-state absorption.[11]

Our results suggest that $\sigma_{1s} > \sigma_{1n}$ for a range of frequencies around 2Δ; however, in the BCS model[12] $\sigma_{1s} < \sigma_{1n}$ because of the coherence of the BCS ground state and the nature of the electromagnetic interaction. Essentially, quasiparticle excitations at the gap have equal amounts of electronlike and holelike character, so that their effective charge is zero. With zero charge, electric dipole matrix elements are also zero. Were a mechanism to exist for replacing the type-II BCS coherence factors, which usually govern electromagnetic absorption, with type-I factors, such as govern sound attenuation, then it would be true that $\sigma_{1s} > \sigma_{1n}$ above the gap.[10] Recently, Fuchs[10] has suggested that the longitudinal dielectric function (which does involve type-I coherence factors) should be used for granular superconductors; its use would lead to superconducting small particles having more absorption than normal ones. However, this model does not enhance the normal-state absorption of small-particle composites.[13] In contrast, our results suggest strongly that the two anomalies stem from identical causes and require identical explanations.

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[6] The purpose of the oxide was to prevent the particles from cold welding together in the bell jar; we do not know the oxide thickness very well although we could distinguish between thin and thick coatings by a color change from black to brown.

[7] N. A. H. K. Rao, J. C. Garland, and D. B. Tanner, to be published.

[8] We have measured the reflectance of our composite samples. To an accuracy of 2% the normal and superconducting samples have identical reflectances. Because the change in transmission typically exceeds 10%, the effect described in this paper does not result from a modified reflectance when superconducting.

[9] In the calculations shown in the inset in Fig. 1 we did not assume the long-wavelength limit; instead we used the more general expression given as Eqs. (3) through (7) of Ref. 4.

[10] See, for example, Michael Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1975).

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[12] Elaborations of the BCS model which are based on phonon emission processes [P. B. Allen, Phys. Rev. B 3, 305 (1971), and 11, 2693 (1975); H. Scher, Phys. Rev. Lett. 25, 759 (1970)] do give rise to slightly higher absorption in the superconducting state, but only at frequencies well above 2Δ (typically at the sum of gap and phonon frequencies). Bulk Pb shows this effect at 40–60 cm^{-1}.

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