ent ν and the relaxation times decrease faster than q^{-2}.

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Heat-Capacity Measurements of the Critical Coupling between Aluminum Grains

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We have measured the heat capacity of granular aluminum specimens with normal-state resistivities ρ_N between 0.6×10^{-3} and 40×10^{-3} Ω cm. The specimens become super-conducting with a heat-capacity transition which is BCS-like for the lowest ρ_N, and then diminishes until it is no longer observable for the highest ρ_N. We conclude that the grains become decoupled such that, because of their small size, they do not exhibit bulk superconductivity when they are isolated.

When aluminum is evaporated in the presence of oxygen it deposits in the form of metallic grains surrounded by insulating oxide. With increasing oxygen pressure the oxide barrier becomes thicker, the grains become increasingly decoupled, and the room-temperature normal-state resistivity ρ_N of the specimen increases. For ρ_N larger than 10^{-4} Ω cm the grain size remains constant at about 30 Å.[1,2]

We have made measurements on a series of granular aluminum films which show that the discontinuity in the heat capacity, which is characteristic of bulk superconductivity, is there to its full extent only in the specimen with the lowest value of ρ_N (0.6×10^{-3} Ω cm). In the specimens with greater ρ_N the change in the heat capacity becomes smaller, and occurs at a lower temperature and over a wider temperature interval, until for the specimen with the highest value of ρ_N (40×10^{-3} Ω cm) it is no longer observable. We were thus able to show that when the grains are isolated they show no heat-capacity transition and that they are, therefore, smaller than the characteristic size below which bulk superconductivity cannot occur in isolated grains.[3-6] In addition, our results show that there is a rather narrow range of values of ρ_N, corresponding to a small change in composition,[7] such that on one side of

it the grains are well coupled, while on the other side they are to a large extent isolated.

The specimens were evaporated from an electron-beam source in a vacuum chamber to which varying amounts of oxygen could be admitted through a needle valve. The rate of evaporation and the thickness were monitored and controlled by an Inficon deposition controller. The rate was kept close to 20 Å/sec and the film thickness was about 10 μm. The substrates for the heat-capacity measurements were water-cooled glass plates with a thickness of about 70 μm, 1 cm wide, and 2 cm long.

During each evaporation a second, bridge-shaped specimen was made for the measurement of the electrical resistance and its transition. The electrical transition temperatures $T_c^{(e)}$ were similar to those previously described for specimens of this kind.[2]

The measurements were made with a pulse method which we have described earlier.[8,9] Some improvements have been made since, such as the use of a more sensitive ac bridge for the detection of the specimen temperature. The size of the temperature change of the specimen thermometer during a heat pulse was kept below 15 mK, and, near the transition, usually considerably lower. In each case the heat capacity of the substrate was measured in a subsequent run after washing off the specimen.

The heat capacity of each specimen was plotted as C/T against T^2 for the separation of the electronic and lattice components. The value of the electronic component in the normal state, C_{en}, is assumed to be proportional to the temperature and is used to calculate the ratio C_{es}/C_{en} of the electronic heat capacities in the superconducting and normal states.

Figure 1 shows the results for four specimens. On each graph we also show the BCS curve calculated for the transition temperature $T_c^{(c)}$, defined as that for which the experimental heat capacity has changed by half the amount of the experimental maximum.

The curve for the 0.6×10^{-3}-Ω-cm specimen is seen to follow the BCS curve very closely. This demonstrates that the specimen behaves like a homogeneous metal, with a sharp transition which is, moreover, close to that which is measured electrically. In these respects the specimen is obviously much better than those for which heat-capacity results have been published previously.[8,10] We therefore have reason for considerable confidence in our method of specimen prepara-
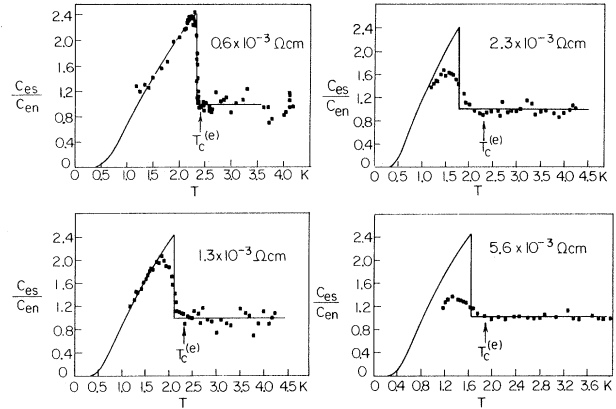

FIG. 1. The ratio of the electronic heat capacities in the superconducting and normal states for four specimens. The full lines are the BCS curves for a transition temperature $T_c^{(c)}$ at which half of the experimental heat-capacity transition has taken place. $T_c^{(e)}$ is the electrical transition temperature.

tion and in our experimental procedure.

The other curves show that as ρ_N increases $T_c^{(c)}$ goes down and the heat-capacity transition diminishes. In another specimen, with 40×10^{-3} Ω cm, the heat-capacity transition is too small to be observed in our experiment, i.e., less than about 15% of the BCS value. An electrical transition remains at 1.90 K, with a width $(10-90)\%$ of 0.54 K which we believe to be determined by the fluctuations. The electrical properties of this specimen have been discussed in a recent publication.[11]

It may also be seen that $T_c^{(c)}$ is always smaller than the electrical transition temperature $T_c^{(e)}$, with a difference between the two which tends to be greater in the high-resistivity specimens.

Our central result is that the heat-capacity transition disappears as ρ_N goes approximately from 10^{-3} to 10^{-2} Ω cm. We conclude that in this region the grains become progressively decoupled, and that they are too small to become superconducting when they are sufficiently isolated.

The notion that there is a characteristic volume below which a specimen cannot have the properties of a bulk superconductor has been considered theoretically by a number of authors.[3-6] The basic idea is that when the volume decreases the thermodynamic fluctuations increase and prevent a thermodynamic transition. A characteristic volume, V_c, is reached when the difference in free energy between the normal and superconducting states is equal to kT_c. The value of V_c is equal to $1/N(0)kT_c$, where $N(0)$ is the normal

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density of states at the Fermi level. For our system V_c is about $(50 \text{ Å})^3$.

The heat capacity of an isolated grain has been explicitly calculated by Mühlschlegel, Scalapino, and Denton (MSD).[6] The MSD curves of heat capacity against temperature for grains of different size (Ref. 6, Fig. 7) show a remarkable similarity to our curves. Each of our curves corresponds to a curve for isolated grains of a certain size, which we can consider to be an effective size which characterizes the intergrain coupling in our specimens. For a volume equal to V_c, the calculated change in the heat capacity is about 3% of the bulk value, which is entirely consistent with our results.

The coupling between grains has been considered in Ref. 5, using a model in which a simple-cubic lattice of spherical grains is embedded in an insulating matrix, with Josephson coupling between the grains. In this paper[5] the region in ρ_N which separates the strong-coupling and the weak-coupling regimes is calculated to be approximately between 10^{-3} and $10^{-2} \, \Omega$ cm, in excellent agreement with our experiment.

In a recent paper[12] Abeles has pointed out that the model of Ref. 5 is incomplete in that it ignores the electrostatic energy E_c which results from electron transfer between grains. This energy tends to decouple the grains, counteracting the Josephson coupling energy E_J.

A more complete calculation has been made by de Gennes,[13] using a model Hamiltonian for the granular system where a "spin" $S_i = 1$ is associated with each grain, with a component S_z which is ± 1 if it is charged as the result of an added or missing pair, and 0 if it is electrically neutral. He shows that there will be a superconducting transition as long as E_c is smaller than mE_J, where m is the number of neighboring grains. Similar conclusions were reached independently by McLean and Stephen.[14]

The value of E_c can, in principle, be calculated with the aid of the model of Abeles and co-workers,[15,16] which gives $E_c = (e^2/\epsilon_1 r)[s/(r+s)]$, where ϵ_1 is the dielectric constant of the insulator, r is the radius of the grain, and s is the distance between grains. The result, however, depends very sensitively on the value of s, especially for specimens near the percolation threshold, where s and E_c go to zero. We therefore prefer to estimate E_c by fitting the normal-state conductivity to the expression of Abeles and co-workers,[16,17] $\sigma = \sigma_0 \exp[-2(C/kT)^{1/2}]$, with C equal to $2\chi s E_c [1 + 1/2\chi s]$ where χ^{-1} is the de-cay length of the metallic wave function in the oxide.

From the data for the specimen with $\rho_N = 5.6 \times 10^{-3} \, \Omega$ cm between 4 and 8 K, we find $C = 5 \times 10^{-6}$ eV. Then $E_c \lesssim 5 \times 10^{-6}$ eV with an exact value which depends on the choice made for the parameter χs.

We calculate E_J from the expression of Ambegaokar and Baratoff[18] and find, for $\rho_N = 5 \times 10^{-3} \, \Omega$ cm and $d = 3 \times 10^{-7}$ cm, a value of about 6×10^{-5} eV.

If we choose m to be 8, we get $mE_J = 5 \times 10^{-4}$ eV and come to the conclusion that electrostatic effects cannot be important in specimens with ρ_N up to $5 \times 10^{-3} \, \Omega$ cm. As ρ_N goes up, the charging energy gets larger, and may play a significant role in the eventual disappearance of superconductivity.

Preliminary measurements of the magnetic susceptibility[19,20] show that the superconductivity retains its three-dimensional character for films up to values of ρ_N of $40 \times 10^{-3} \, \Omega$ cm. The details of the remaining "bulk" superconductivity remain to be explored. It may be, as is already evident from Ref. 6, that the susceptibility and the heat capacity are influenced quite differently by the thermodynamic fluctuations.

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New Hybrid Photoconductivity Technique for the Investigation of CO_2-Laser–Induced Hot-Carrier and Free-Carrier Absorption Effects in Degenerate n-InSb at 1.8 K

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Free-carrier absorption of tuned CO_2-laser radiation is shown to be a valuable new tool for the extraction of information on photoheated hot carriers and the free-carrier absorption coefficients in low-concentration, degenerate n-InSb at liquid helium temperatures. The technique exploits parallel photoheating and dc-heating experiments conducted in a regime where conductivity changes are unambiguously determined by mobility changes.

Illumination of semiconductors with intense laser radiation leads to carrier heating.[1,2] Studies of hot-carrier distributions are important because they yield information concerning the electron-electron and electron-phonon interactions in semiconductors. Here, we report for the first time free-carrier absorption-induced photoconductivity measurements on degenerate n-InSb under optical excitation at CO_2-laser wavelengths that allow extraction of electron temperatures. Furthermore, we present the results of a unique combination of independent electrical and laser experiments carried out at liquid helium temperatures on the same low-concentration sample of n-InSb, that allows, in principle, the precision extraction of the free-carrier absorption coefficient as a function of CO_2 laser frequency and laser power. These absorption coefficients are so small at 10 μm that their determination from classical optical absorption measurements alone would prove impractical. Consequently, these novel hybrid experiments and their interpretation result in the *first* reported estimates for the free-

carrier absorption coefficient of low-concentration (1.4×10^{15} cm^{-3}) n-InSb.

Figure 1 shows a block diagram of the equipment used in this experiment. The sample, immersed in liquid helium in a variable-temperature optical Dewar, was illuminated with a laser pulse produced by mechanically chopping a beam (TEM_{00} mode) from a grating-tuned cw CO_2 laser which provided single-line outputs of several watts from ~9.2 to ~10.9 μm. In the present experiments, a laser pulse with a width of ~20 μsec [FWHM (full width at half-maximum)], a rise and fall time of ~2 μsec, and a repetition rate of ~1700 Hz were employed. The laser pulse was positioned to illuminate the region of the sample between the potential contacts. Calibrated filters of either CaF_2 sheets or sheets of Teflon or some combination of both were used for attenuation.

Figure 2 shows comprehensive results obtained from three separate experiments on how the mobility changes with (1) applied electrical power P_E per electron (obtained from electrical heating