

Thermodynamic transition of small superconducting particles

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Measurements are presented which show that the specific heat of small tin particles exhibits a BCS-like structure at the superconducting transition even if the particle size is much smaller than the superconducting coherence length. This structure remains, broadened by fluctuation effects, down to dimensions so small that size quantization produces an electronic energy level spacing larger than the superconducting energy gap. Our results suggest that this energy ratio determines the crossover from bulk behavior (with a well-defined phase transition) to zero-dimensional behavior (with no superconducting order).

This paper is a report of specific-heat measurements of the superconducting transition of small Sn particles. Our interest in small superconducting particles is motivated by the idea that long-range order cannot persist into the zero-dimensional limit.¹ The effective dimensionality of a material is set by the ratio of its length, width, and height to some characteristic length scale. In a superconductor, there are two relevant lengths. The first is the zero-temperature limit of the Ginzberg-Landau coherence length $\xi(0)$, which determines the particle size below which thermodynamic fluctuations become important. It is well established that fluctuations broaden both the thermodynamic and resistive transition of a superconductor,² and for this reason it is commonly assumed that the crossover from bulk to zero-dimensional behavior of superconducting particles is set by this scale. The coherence length in the dirty limit is $\xi(0) = 0.85(\xi_0 l)^{1/2}$, where l is the mean free path, equal to the particle radius, and ξ_0 is the Pipard coherence length, about 2000 Å for Sn.

However, a second view³⁻⁵ is that long-range order, although diminished by fluctuations, may persist to sample dimensions well below $\xi(0)$. According to this view, the crossover to zero dimensionality occurs at the particle size at which the spacing between electronic energy levels δ becomes comparable to the zero-temperature energy gap $\Delta(0)$. In small particles, the electronic energy spectrum is quantized into nearly nondegenerate discrete levels whose spacing at the Fermi energy is given approximately by ϵ_F/N , where ϵ_F is the Fermi energy and N is the number of conduction electrons in the particle. This criterion suggests that superconductivity in Sn would vanish for particle diameters below about 50 Å.

Our measurements of the thermodynamic transition in nearly isolated Sn particles support the idea that superconductivity is a remarkably persistent phenomenon, evident in particles whose diameter is much smaller than the superconducting coherence length. These measurements are the first to map the transition from bulk superconducting behavior of large particles, through the fluctuation-

weakened regime of particles smaller than the coherence length, to the destruction of superconductivity in particles so small that their level spacing exceeds the gap energy.

The samples consisted of oxide-coated spherical Sn particles loosely compressed into a pellet. The particles were made by evaporating Sn into a 300-mTorr inert-gas atmosphere containing 50 mTorr partial pressure of oxygen. The inert gas was argon for particle diameters greater than 200 Å, and helium for smaller particles. By controlling pressures and evaporation rates, average particle diameters for a given batch could be varied from 30 to over 1000 Å. The distribution of particle sizes from each batch was measured with an electron microscope and was used to compute an average particle volume for each sample,

$$V = \sum_i n_i \frac{4}{3} \pi (r_i)^3 / \sum_i n_i, \quad (1)$$

where n_i is the number of particles with radius r_i . [The effective particle diameter $\langle d \rangle = (6V/\pi)^{1/3}$ inferred from the average volume was typically 10% larger than the average diameter.] In general, particle diameters were found to vary about a factor of 2 in each batch, with an approximate log-normal distribution. The samples were made by gently compacting the oxide-coated Sn particles into a solid pellet in an evacuated die. Typical sample dimensions were $2 \times 2 \times 0.25$ mm³. The density of the compacted solid was about 0.4 of the density of bulk Sn, with a resistivity of about 10^8 that of Sn.

The heat capacity of the small-particle samples was measured using an ac calorimeter.^{6,7} Approximately 10 mg of the sample was clamped between two 12-mm-diam by 0.1-mm-thick sapphire disks. A gold film heater was evaporated onto one disk while an Au:Fe-Cu thermocouple was spot-welded to the other. With the reference thermocouple junction anchored to the helium bath, the calorimeter allowed heat-capacity measurements to be made between 2 and 5 K with a resolution of better than 0.1%. The heat capacity of the bare calorimeter (about

40% of the total at 4 K) was measured separately and subtracted from the data. The calorimeter was calibrated by comparing the measured heat capacity of bulk Sn with published values of the heat capacity.

Figure 1 shows the total heat capacity C_v of a typical Sn small-particle sample between 2.8 and 5.0 K. The onset of superconductivity in these particles, whose effective diameter was $\langle d \rangle = 505 \text{ \AA}$, leads to a rise in the heat capacity at $T_c \approx 3.7 \text{ K}$. In order to isolate the electronic specific heat C_e , it is necessary to subtract the lattice contribution to C_v . The total specific heat of bulk Sn in the normal state (below 4.2 K) is known⁸ to obey the expression

$$C = \gamma_1 T + \beta T^3 + \alpha T^5 + \delta T^7. \quad (2)$$

In Eq. (2) the linear term is the normal electronic contribution, while the T^3 , T^5 , and T^7 terms correspond to the lattice specific heat. Our calibration data on bulk Sn are in excellent agreement with published⁸ values below 4.2 K, although a slightly better fit was obtained up to 5 K by increasing δ by a factor of 3. Because our data on small particles showed some sample-to-sample variation in γ and β , we chose those values of γ and β for each sample which gave the best fit to our data in the normal state. The solid line in Fig. 1 illustrates the agreement of the data with Eq. (2).

Figure 2 shows the electronic contribution to the heat capacity of bulk Sn and of five small-particle Sn samples whose effective diameters ranged from 73 to 505 \AA . To facilitate comparison among different samples, the data are normalized to γT_c , the electronic specific heat at T_c , and to the reduced temperature T/T_c . Each sample in Fig. 2 is also labeled with an estimate of the electronic energy level spacing $\delta = 1/N(0)V$ [normalized to $\Delta(0) = 1.75k_B T_c$], where $N(0)$ is the single spin density of states per unit volume evaluated at the Fermi energy⁹ and V is the average particle volume. The values of T_c for the two samples with largest particles were determined empirically by comparing the specific-heat data below T_c with the data for bulk Sn. For the three samples with the

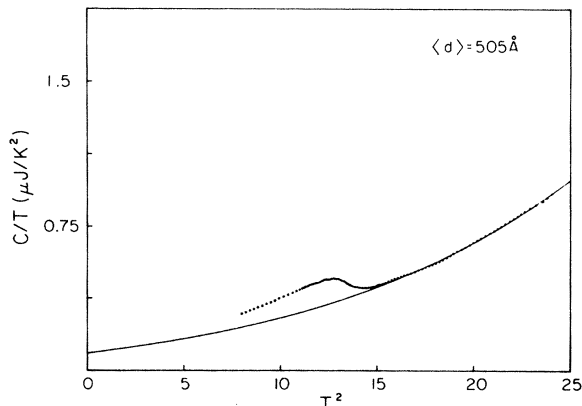


FIG. 1. Total heat capacity of Sn small particles vs the square of the temperature. Data are shown as points while a fit of the normal-state data to a power series [Eq. (2)] is shown as the solid line.

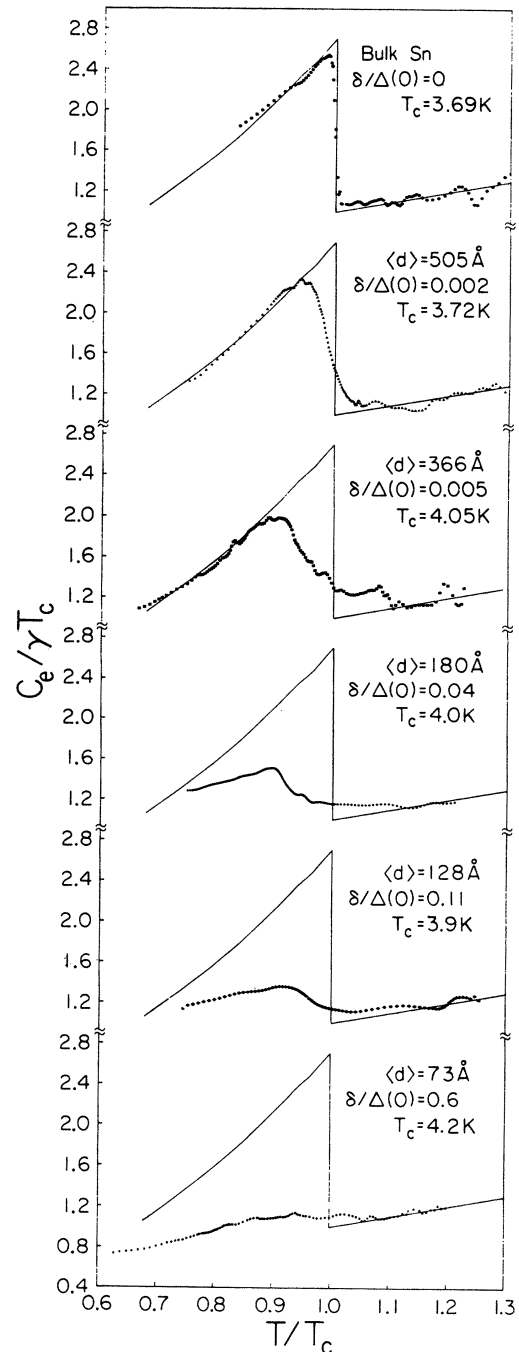


FIG. 2. Electronic heat capacity vs reduced temperature for bulk Sn and five samples of Sn small particles. Solid line corresponds to the expected heat capacity for bulk Sn.

smallest particles, T_c was arbitrarily chosen as the temperature at the midpoint of the rise in C_e .

The solid lines in Fig. 2 correspond to the measured⁸ electronic specific heat of bulk Sn. (Data on the bulk Sn differs from the theoretical BCS heat capacity in that the discontinuity at T_c and the heat capacity well below T_c are both larger than predicted.) Although broadened by fluctuations near T_c , the specific heat of the sample with the largest particles, for which $\xi(0) \approx 600 \text{ \AA} \approx \langle d \rangle$, is equal to the bulk value below $0.9T_c$. The next-to-largest

sample is qualitatively similar. In the three smaller samples, the transition is not only broadened but substantially weakened in amplitude. In the sample with smallest particles, for which $\delta/\Delta(0)=0.6$ and $\xi(0)\approx 230 \text{ \AA} \approx 3\langle d \rangle$, the transition is nearly absent. One may conclude, therefore, that the disappearance of superconductivity (i.e., the crossover to zero dimensionality) is determined by the influence of size quantization of electronic states in the particles.

The effect of fluctuations on the heat capacity of isolated small particles has been calculated by Mühlischlegel, Scalapino, and Denton¹⁰ (MSD) as a function of particle volume. Their calculations, based on a Ginzburg-Landau formalism, are expected to be valid for particles that are small compared to the coherence length ($d \ll \xi_0$), yet sufficiently large so that size quantization of levels can be neglected [$\delta \ll \Delta(0)$]. Both of these criteria are satisfied in our two samples with the largest particles. Because the MSD formalism is appropriate only near T_c , we have modified their calculations slightly—according to a suggestion by Patton, Lamb, and Stroud¹¹—by assuming an explicit temperature dependence for the coefficients a and b of the $|\psi|^2$ and $|\psi|^4$ terms in the Ginzburg-Landau free energy. This modification permitted us to compare our data to the MSD results over a wider temperature range.

Specifically, the coefficients used in our analysis were $a=N(0)\bar{a}$ and $b=2N(0)\bar{b}/(\pi k_B T_0)^2$, where T_0 is the thermodynamic transition temperature, $\bar{a}=(t^2-1)/(t^2+1)$, $\bar{b}=4(0.526)/(t^2+1)^2$, and $t=T/T_0$. With these coefficients, the superconducting heat capacity can be written

$$C_e = \gamma T_0 \left[\left(2t \frac{dy}{dt} + t^2 \frac{d^2y}{dt^2} \right) \left(2y - \frac{2}{\sqrt{\pi}} Z_0^{-1} \right) + t^2 \left(\frac{dy}{dt} \right)^2 \left(2 + \frac{4y}{\sqrt{\pi}} Z_0^{-1} - \frac{4}{\pi} Z_0^{-2} \right) \right], \quad (3)$$

where $y=(\bar{a}\pi/2)[1.76\bar{b}t\delta/\Delta(0)]^{-1/2}$ and $Z_0^{-1}=\exp(y^2) \times [1 \pm \text{erf}(y)]$. The upper sign is used for $y < 0$ and the lower for $y > 0$. This expression reduces to the MSD result for the usual choice of $\bar{a}=t-1$ and $\bar{b}=0.526$. In fitting our data, we have used $\delta/\Delta(0)$ and T_0 as adjustable parameters (γ is determined from the measured normal-state heat capacity).

Figures 3(a) and 3(b) show the superconducting heat capacity near T_c for the two samples with mean particle diameters of 505 and 366 Å, respectively. The solid line in each figure is the best fit of Eq. (3) to the data, with the values of $\delta/\Delta(0)$ and T_0 indicated on the figures. In both cases, the value of T_0 obtained by the fit differs by less than 3% from the experimental value of T_c . Similar agreement was obtained for the inferred level spacing $\delta/\Delta(0)$, which for each sample corresponds to a diameter that is within 15% of the measured value. To our knowledge, the data on these two samples represent the first quantitative test of the MSD theory. The good agreement supports our belief that the small particles in our samples are so weakly coupled that their heat capacity

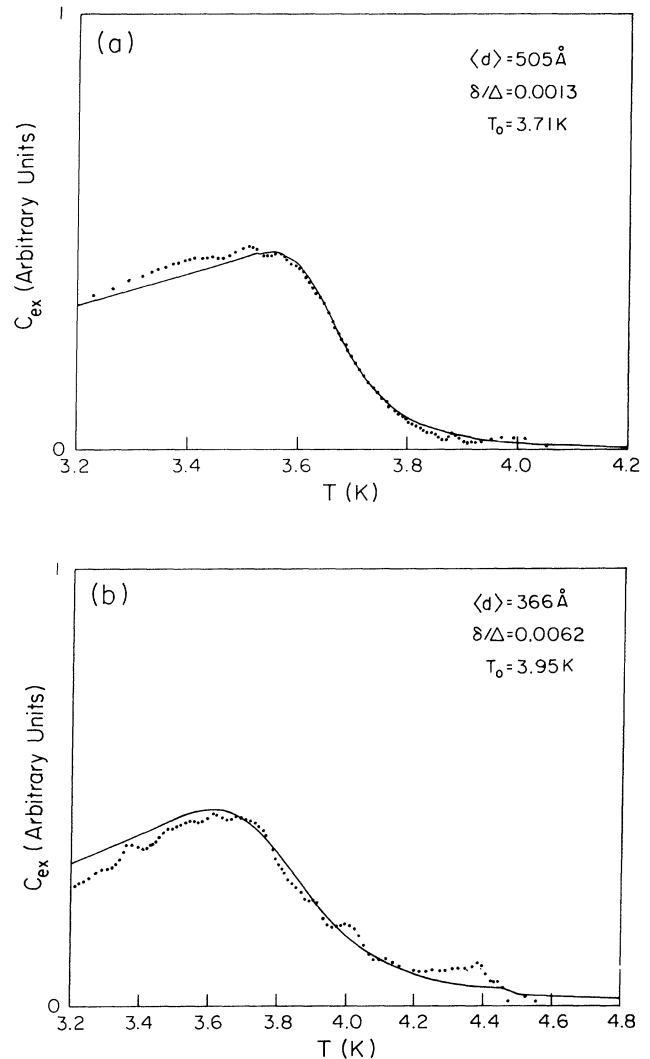


FIG. 3. Excess heat capacity ($C_e - \gamma T$) vs temperature. Data are shown as points and the fit to Eq. (3) is shown as a solid line. (a) is for 505-Å-diam particles while (b) is for 366-Å-diam particles.

is indicative of their actual sizes.

In our three samples with the smallest particles, δ is no longer small compared with $\Delta(0)$. Ginzburg-Landau theory cannot deal adequately with the quasiparticle contributions to the thermodynamic phase transition in this regime. However, numerical heat-capacity calculations¹⁰ using the microscopic theory (see Fig. 7 of MSD) agree qualitatively with our measurements. The agreement includes the way in which the heat-capacity jump at the transition broadens and decreases in height as the particle diameter becomes smaller and the fact that this jump is almost gone when $\delta \approx \Delta(0)$. The only point of disagreement is that the measured heat capacity remains lower than the bulk value when T is far below T_c , while the calculated value does not. This discrepancy may result either from the details of the level distribution (MSD assume equally spaced levels) or from size effects in the phonon spectrum. (Phonons whose wavelength exceeds the particle diameter should be forbidden, leading to a reduction in

the lattice contribution to C_v at low temperatures; this effect was not included in our background term.)

These measurements are the first investigation of the effects of particle size on the thermodynamics of the superconducting phase transition. Although our data and the heat capacities of granular aluminum films reported by Worthington *et al.*¹² appear very similar, the physical effects governing the superconducting transition are completely different in the two materials. The grains in granular aluminum films are always very small, and the intergrain coupling is the quantity which is affected by variations in sample-preparation conditions. The superconducting transition is sharp when the grains are strongly interacting and becomes smeared when the coupling is reduced. In contrast, the heat capacity of our samples is controlled by the size of the individual isolated particles. Buhrman and Halperin¹³ have measured the magnetic susceptibility of isolated aluminum particles, having $d \approx \xi_0$, and found good agreement with the calculations of MSD. However, because the superconducting transition does not affect the susceptibility when the diameter is small compared with the penetration depth, it was not possible to investigate the regime dominated by size quantization. Our data also resemble those of Tsuboi and Suzuki,¹⁴ who studied the heat capacity of an evaporated Sn/SnOx com-

posite film. However, their system differed significantly from ours in that the Sn islands in their films were always larger than 250 Å in diameter ($\bar{\delta} \leq 0.025$) and showed evidence of significant intergrain coupling.

In summary, our results indicate that the heat capacity of small superconducting particles is very similar to the bulk heat capacity even when the particle diameter is smaller than the zero-temperature dirty-limit coherence length. Superconductivity is destroyed only at much smaller sizes, where the spacing between the electronic energy levels becomes comparable to the energy gap; at that point, the particle gains no energy advantage in becoming superconducting because there is already a gap in the electronics spectrum. For Sn, this zero-dimensional limit occurs when $d \approx 70$ Å (corresponding to about 10^4 electrons in a single particle). By the time that $d \approx 200$ Å (10^5 electrons) the superconducting transition is well established.

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