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Measurement of the specific-heat anomaly at the superconducting transition of $YBa_2Cu_3O_{7-\delta}$

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The specific heat of the ceramic superconductor $YBa_2Cu_3O_{7-\delta}$ has been measured in the vicinity of the transition temperature $T_c = 90$ K, using a combination of ac and heat-pulse calorimetry. A step change $\Delta C_p = 6.2$ mJ/gK is observed at T_c which, when divided by the electronic contribution to the heat capacity estimated from susceptibility data, gives a value close to that expected from Bardeen-Cooper-Schrieffer (BCS) theory. These results confirm that the material is a bulk superconductor with BCS-like behavior. The lattice contribution can be fitted to a Debye specific heat with $\Theta_D \approx 440$ K.

Apart from high-transition temperatures, little distinguishes the superconductive properties of the new ceramic materials[1-3] from more prosaic superconductors. On a diagram which locates each material on a plot of the electronic specific-heat coefficient γ versus critical temperature T_c, however, the new superconductors lie well above the range occupied by other materials.[4] To date, γ has been inferred from other data, using the free-electron model.[3]

In this Rapid Communication, we report the precise measurement of the jump in the specific heat C_p associated with the superconducting transition in $YBa_2Cu_3O_{7-\delta}$. We find, in summary, the following.

(i) With decreasing temperature, C_p exhibits a steplike increase to a maximum at 90 K, corresponding to the completion of the resistive transition measured on a portion of the same sample.

(ii) Although the resistivity shows some deviations from high-temperature extrapolations near 100 K, no excess specific heat is found above 93 K.

(iii) The ratio of the specific-heat jump to the electronic contribution to the specific heat, as estimated from the Pauli paramagnetism of the sample, is close to the BCS value 1.43.

(iv) There is no evidence for critical behavior; i.e., a logarithmic peak in C_p, such as might be expected from a breakdown of the Ginzburg criterion in these materials.

Each sample was prepared by thoroughly mixing and grinding $BaCO_3$, Y_2O_3, and CuO powders (all 99.999% pure) and reacting them in a platinum crucible in air at 950 °C for 24 h, with two intermediate grindings. The reacted material was ground and pressed into pellets under a pressure of 500 MPa applied for 5 min. After removal from the press, the pellets were heat treated in a stream of pure oxygen for 16 h at 900 °C, cooled to 700 °C in 1 h, held at 700 °C for 16 h, and finally cooled to room temperature over an 8 h period. X-ray diffraction showed each sample to be single phase $YBa_2Cu_3O_{7-\delta}$. Specific-heat measurements were made using a combination of the ac calorimetric method[5] and the standard quasiadiabatic heat-pulse method. The ac sample was a thin disk 3 mm in diameter and 0.5 mm thick with a mass of 18 mg. A larger pellet from the same batch (5 mm diameter, 3 mm thick, mass 268 mg) was used for the heat-pulse method.

For resistivity measurements, a $1 \times 1 \times 5$ mm^3 bar was cut from a pellet using a diamond saw, and fine copper wires attached with silver paint. The sample was thermally anchored to a sapphire substrate and the temperature measured with a calibrated carbon-glass thermometer. Resistivity data, taken only after thermal equilibrium had been established, are shown in Fig. 1. The midpoint of the resistive transition is at 91.6 K, the width between 10% and 90% points is 1.6 K, and zero resistance occurred at 90.1 K.

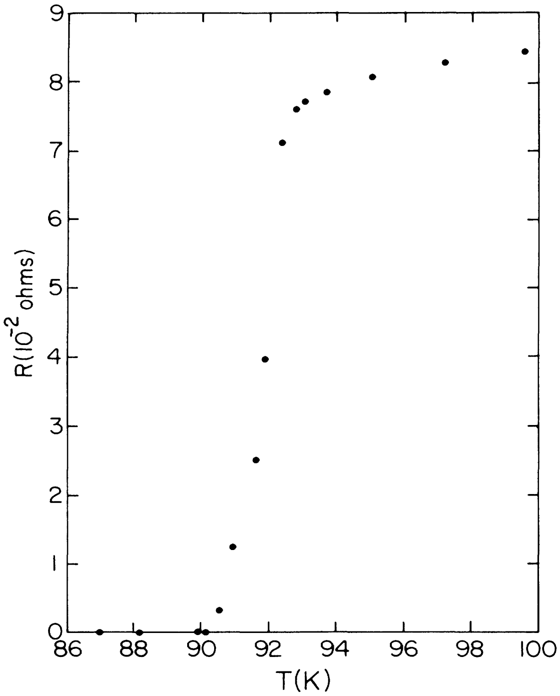

FIG. 1. Resistivity of $YBA_2Cu_3O_{7-\delta}$ from the same batch as the specific-heat sample. Zero resistance is achieved at 90.1 K.

In the ac method, the sample is heated periodically at a frequency whose period is much longer than the thermal diffusion time of the sample but much shorter than the sample-reservoir relaxation time.[6] When these criteria are met, the temperature oscillations are inversely proportional to both frequency and the heat capacity of the sample. In the present experiment, ac heat input to one face of the sample was provided by light from a regulated quartz lamp, modulated by a mechanical chopper. A flattened thermocouple, made from 25 μm diam Chromel and Constantan wires, was attached to the opposite face of the sample with a small amount of thinned GE 7031 varnish. The small temperature oscillations (≈ 5 mK rms) were detected by the thermocouple and recorded with a lock-in amplifier and personal computer. The ac method permits continuous recording of the specific heat as the temperature is slowly varied and gives a signal/noise ratio of 200 or more. The same thermocouple also records the dc temperature offset between the sample and reservoir due to the average power provided by the chopped light. The reservoir temperature is measured by a calibrated carbon-glass thermometer.

Optical heating eliminates addenda from heater and leads—and therefore gives excellent relative heat-capacity data—but does not yield an absolute value of the specific heat. To determine the heat input, we performed an adiabatic heat-pulse measurement at liquid-nitrogen temperature. In this case, a 1 kΩ strain gauge was used as a heater, and the addendum correction due to heater and thermometer (15% of the total) was subtracted. The resulting value (147 ± 7 mJ/g K at 77 K) was used to calibrate the ac data. Use of a single calibration point assumes that the absorptivity of the sample in the infrared and optical region is independent of temperature.

The results of an ac calorimetric scan through the superconducting transition is shown in Fig. 2. The presence of an anomaly at 90 K is clearly visible, amounting to approximately 3% of the total heat capacity. To analyze this, we must subtract the large background heat capacity of the lattice and the normal conduction electrons. The electronic specific heat is calculated from the Pauli paramagnetic susceptibility. Figure 3 shows that susceptibility in the vicinity of T_c for a sample cooled in 21 Oe in a superconducting quantum interference device magnetometer. After subtraction of the core diamagnetism[7] (assuming 7 oxygen atoms and Cu^{2+} cores), this leads to a value $\chi_g = 7.9 \times 10^{-7}$ emu/g Oe. Assuming the free-electron model to hold, we obtain the density of states at the Fermi energy $g(E_F) = 5.4$ states/eV Cu atom, and the electronic specific heat parameter $\gamma = 0.056 \pm 0.002$ mJ/g K^2 (or 12.6 ± 0.4 mJ/mole Cu K^2). The latter is larger than the estimate of Cava *et al.*[3] The density of states is substantially higher than the values calculated by both Mattheiss and Hamann[8] (3 states/eV Cu atom) and by Massida, Yu, Freeman, and Koelling[9] (1.3 states/eV Cu atom).

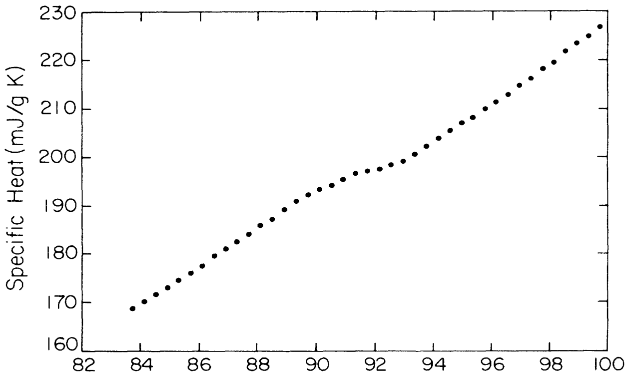

FIG. 2. ac specific-heat data near the superconducting transition of $YBA_2Cu_3O_{7-\delta}$.

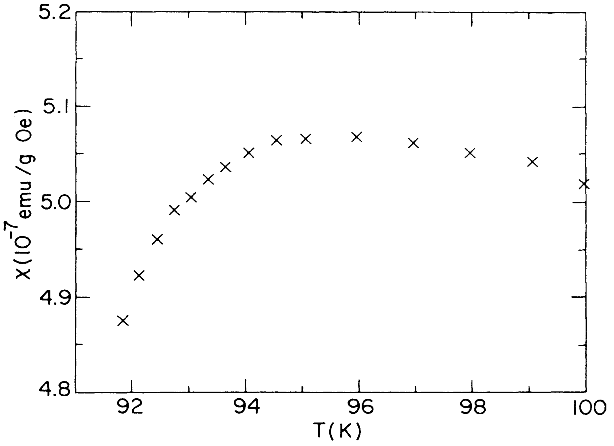

FIG. 3. The magnetic susceptibility in the vicinity of T_c.

For the lattice contribution, we make the assumption that all 13 atoms in the formula unit contribute to a Debye specific heat with limiting value $39R = 324$ J/mole K or equivalently 487 mJ/g K. As is usually the case, the Debye temperature, which is the only adjustable parameter, must be varied slightly, from $\Theta_D = 435$ K at 100 K to 440 K at T_c, to fit the data. As an approximation to the lattice heat capacity, we extrapolate the temperature dependence of Θ_D to lower temperatures and subtract the sum of the Debye contribution and that of the normal electrons from the data. The results are shown in Fig. 4, along with a plot of $\Theta_D(T)$ in the inset. There is no evidence for excess heat capacity above 93 K, and the transition is essentially complete at 90 K, in agreement with the resistivity results in Fig. 1. The jump in specific heat is $\Delta C_p = 6.2 \pm 0.1$ mJ/g K. The ratio

$$\Delta C_p/\gamma T_c = 1.23 \pm 0.08 \qquad (1)$$

is close to the value 1.43 expected from the BCS model. Because they show a complete Meissner effect (flux exclusion), we have assumed that the samples become completely superconducting. Possible differences between specific-heat and susceptibility-effective masses have been ignored. Conversely, our results strongly suggests that the superconductivity in $YBa_2Cu_3O_{7-\delta}$ *is* a bulk effect and that the BCS model accurately describes the transition.

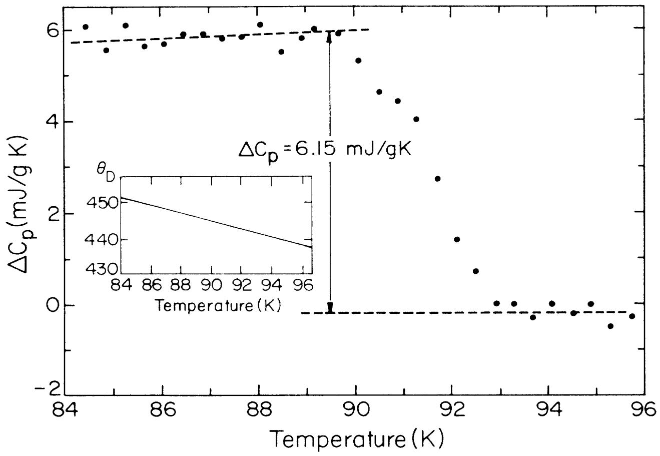

FIG. 4. Excess specific heat in the vicinity of 90 K. The lattice specific heat, modeled as a Debye contribution with the Debye temperature shown in the inset, and the electronic specific heat, with $\gamma = 5.6 \times 10^{-2}$ mJ/gK^2, have been subtracted. The jump is $\Delta C_p = 6.2$ mJ/gK.

Note that since the ratio in Eq. (1) is less than the BCS value, the specific heat does not support a strong-coupling model for these high-T_c superconductors.[10]

In ordinary superconductors, the zero-temperature correlation length $\xi(0)$ is very long, on the order of 10^3 Å. This causes the width of the critical region, as given by the Ginzburg criterion[11]

$$\delta T/T_c \approx [k_B/\Delta C_p \rho \xi(0)^3]^2 , \qquad (2)$$

to be very small; here ρ is the density. For $YBa_2Cu_3O_{7-\delta}$, however, $\xi(0)$ has been estimated[3] to be on the order of 20 Å, raising the possibility that true critical behavior be seen in these materials. Using our value for ΔC_p and $\xi(0) = 20$ Å, we find that $\delta T/T_c \approx 2 \times 10^{-3}$ meaning that mean-field behavior should be observed only further than 0.2 K from T_c. However, we see no evidence for a logarithmic term in the specific heat, such as would be expected for a two-component order parameter. As more perfect materials become available, it is possible that critical point behavior associated with superconductivity could be observed.

Subtraction of the lattice specific heat is a major obstacle in analyzing the superconducting contribution to the heat capacity. We have used a Debye model with a temperature-dependent Θ_D, which is a serious oversimplification. Neutron data on the phonon density of states[12] suggest a Debye-like spectrum that peaks near 250 K plus a number of other peaks at higher temperatures. Our estimate of 440 K falls near a minimum between acousticlike and opticlike portions of the phonon density of states. If, instead of a temperature-dependent Θ_D, we had fixed the Debye temperature at $\Theta_D = 440$ K, the excess specific heat in Fig. 4 would decrease more strongly, passing through zero (i.e., γT) near 77 K.

The plot of critical temperature versus electronic specific-heat constant γ, as noted above, suggests that oxide superconductors belong to a class different from both heavy-fermion superconductors and more "normal" metallic materials.[4] Our result, $\gamma = 37$ mJ/mole K,[2] lies on the line formed by $Ba(Pb,Bi)O_3$ and $(La,Sr)_2CuO_4$, on the low-density-of-states side of the diagram. (The original[4] figure is located $YBA_2Cu_3O_{7-\delta}$ on a per-mole-Cu basis.) What is more, $\Delta C_p/\gamma T_c$ is below the BCS weak-coupling limit, although this could result from an anisotropic energy gap.[13] It seems quite likely that the low electronic density of states, ordinary Debye temperature, absence of evidence for strong coupling, and the failure to find an isotope effect[14] point to a new coupling mechanism for superconductivity in this material.

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