Specific Heat of Single Crystals of $YBa_2Cu_3O_{7-\delta}$: Fluctuation Effects in a Bulk Superconductor

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Gaussian fluctuations have been observed in the specific heat of two single crystals of $YBa_2Cu_3O_{7-\delta}$. Deviations from a BCS-type step are well accounted for by 3D Gaussian fluctuations whose amplitude ratio, in the cleaner sample, implies that the number of order-parameter components is 7 ± 2. This result is inconsistent with an O(2) Ginzburg-Landau theory.

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In the rush to understand the mechanisms leading to superconductivity at 90 K, there has been a tendency to overlook important aspects of the superconducting properties of these materials. For example, the BCS coherence length[1] $\xi_0 \approx 10$ Å is orders of magnitude smaller than that of "ordinary" superconductors. This, along with the high transition temperatures, means that long sought after fluctuations, previously studied in thin films where the reduced dimensionality enhances the effects, should be readily observable in the bulk.[2,3] Recently, the precursive decrease in resistivity and susceptibility was attributed[4,5] to three-dimensional Gaussian fluctuations of short-lived Cooper pairs. This has permitted the extraction of values of H_{c2} and ξ_0 that are in agreement with other estimates.[5] Because these studies were performed on polycrystalline samples, the possibility remains that inhomogeneities (e.g., superconducting filaments or loops) contribute significantly to the rounding of the resistive and magnetic transitions. In this Letter, we report the observation of fluctuations in a thermodynamic quantity—the specific heat C_p—both above and below T_c, in two single crystals of $YBa_2Cu_3O_{7-\delta}$. This is the first observation of the specific-heat anomaly in a single crystal of the high-temperature superconductor and, we believe, the first observation of Gaussian fluctuations in the specific heat at a 3D superconducting transition. The extensivity of the specific heat, of course, renders it relatively insensitive to minute volume fractions of superconducting material.

One single crystal was grown at Argonne National Laboratory with methods described elsewhere.[6] The extremely small single crystal (234 μg, $0.3\times0.3\times0.5$ mm^3) was mounted on a thermocouple formed from flattened 12-μm-diam Chromel and Alumel wires with a small amount of GE varnish. Preliminary results obtained on a larger (600 μg) crystal grown at the University of Illinois are also presented. A standard ac calorimetric method, described previously,[2] was used. The exposed (001) face was darkened with DAG colloidal graphite to avoid changes in light absorption. Data in the vicinity of $T_c = 89$ K are plotted as C_p/T in Fig. 1; the superconducting contribution of the Argonne sample is less than 2% of the total specific heat. In addition to the main transition, there is a small, reproducible anomaly at 93 K. This is much less evident in the Illinois crystal; it is possible that two superconducting compositions are present or that there is a structural transition above T_c.[7] Data were taken by our slowly increasing the sample temperature (≈ 0.1 K/min) while continuously digitizing the temperature and specific-heat signal on a personal computer. Digital averaging over 0.1-K temperature intervals resulted in the data set shown. The noise is primarily due to Johnson noise of the sensor-amplifier chain.

The large BCS coherence length ξ_0 of ordinary 3D su-

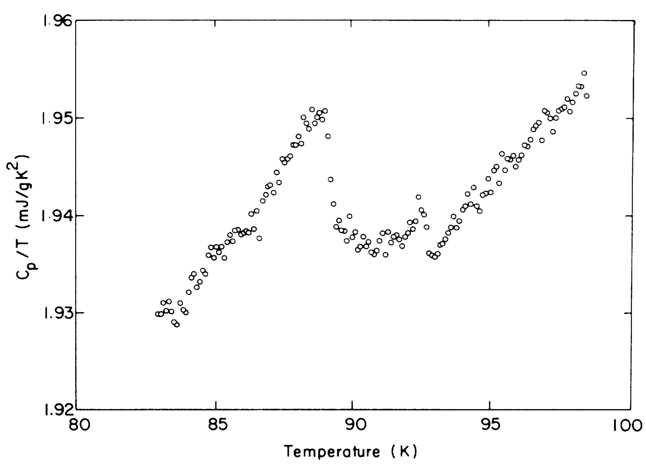

FIG. 1. Specific heat C_p of the Argonne crystal divided by absolute temperature vs temperature. The feature at 89 K is associated with the onset of superconductivity. The smaller anomaly at 93 K is reproducible and is discussed in the text.

perconductors means that mean-field theory is valid to extremely small values of $t = T/T_c - 1$. Thus, the specific-heat jump predicted by the BCS theory is universally observed. Its magnitude may be modified by strong-coupling corrections, but critical behavior is not found. Thouless[8] and subsequently Aslamazov and Larkin[9] predicted that, even in the mean-field regime, there is a Gaussian contribution to the specific heat above (+) and below (−) T_c, given by

$$\Delta C = C^{\pm}(\pm t)^{-(2-d/2)} \tag{1}$$

with

$$C^{+} = k_B/8\pi\xi_{GL}(0)^3, \tag{2}$$

and $\xi_{GL}(0)$ the $T=0$ Ginzburg-Landau coherence length. For quadratic fluctuations about mean-field theory in an $O(n)$ model, the amplitudes are in the ratio[10]

$$C^{+}/C^{-} = n/2^{d/2}, \tag{3}$$

where n is the number of components of the order parameter and d is the dimensionality. It can be shown that electromagnetic interactions between fluctuations make a negligible correction to Eq. (3) for extreme type-II superconductors. For $d=3$ and $n=2$, the case of a conventional superconductor, we expect $C^{+}/C^{-} = 1/\sqrt{2}$. An early but unsuccessful attempt to observe these effects was reported by Cochran.[11] Note that even with the small Ginzburg-Landau coherence lengths expected[1] for $YBa_2Cu_3O_{7-\delta}$, the Ginzburg criterion for $n=2$,

$$|t| \equiv |T/T_c - 1| \gg (1/32\pi^2)(k_B/\Delta C\xi_0^3)^2, \tag{4}$$

predicts that critical effects (logarithmic divergence) should not be observable for $|t| > 10^{-3}$. The Gaussian components are in addition to the usual BCS contribution, which we take to be of the form (for $T < T_c$)

$$C_{BCS}/T = 1.43\gamma_{eff}(1 + 1.83t). \tag{5}$$

Here, γ_{eff} includes any strong-coupling corrections, and the temperature-dependent term is obtained from a fit to Mühlschlegel's numerical results[12] over the experimental range of reduced temperature.

The data of Fig. 1 for the Argonne sample include a large lattice contribution, the normal electronic component, and the superconducting contributions $\Delta C/T$ and C_{CBS}/T. The lattice and electronic contributions may be represented by a linear (in reduced temperature t) background. We treat C^{+} and γ_{eff}, as well as the magnitude and slope of the background, as adjustable parameters in a least-squares fit to the data. We make no assumption that the mean-field discontinuity is necessarily as predicted by the BCS theory. We vary the ratio C^{+}/C^{-} and T_c manually to reduce the number of fitting parameters, while inspecting log-log plots of the data to be sure that the specific-heat singularity is indeed a power law with the same exponent above and below t_c. In Fig. 2, we have plotted the data for the Argonne sample with the best-fitting background subtracted, for which $C^{+}/C^{-} = 2.8$ and $T_c = 88.95$ K. The BCS-type contribution (dashed curve) and the sum of BCS-type and fluctuation contributions (solid curve) are also shown. The dash-dotted curve is the best fit that can be obtained on the assumption of a t^{-1} fluctuation contribution, as expected for $d=2$.

The fit of Fig. 2 gives a value

$$1.43\gamma_{eff}T_c = 14 \pm 3 \text{ mJ/cm}^3\text{ K} \tag{6}$$

for the specific-heat jump, if we assume a density of 6.4 g/cm^3. The comparable value for the Illinois sample is 36 ± 2 mJ/cm^3 K, which agrees with our value[2] of 40 ± 4 mJ/cm^3 K for a polycrystalline sample. A fraction $f = 14/40 = 0.35$ of the Argonne sample undergoes a superconducting transition at this temperature. Indeed shielding measurements[13] on the same crystal show a plateau near 60 K that is absent in the Illinois sample. The amplitude C^{+} is 1.6 ± 0.3 mJ/cm^3 K for the Argonne sample (after scaling up by $1/f$) and 2.0 ± 0.1 for the Illinois crystal. We choose the mean value

$$C^{+} = 1.8 \pm 0.3 \text{ mJ/cm}^3\text{ K}. \tag{7}$$

The substitution of this value into (2) gives

$$\xi_{GL}(0) = 7 \pm 0.5\ \text{Å}, \tag{8}$$

which agrees with independent estimates[1] based on a Ginzburg-Landau analysis of critical-field data for polycrystals.

In the above analysis, we have assumed that $YBa_2Cu_3O_{7-\delta}$ is a 3D superconductor. In order to ex-

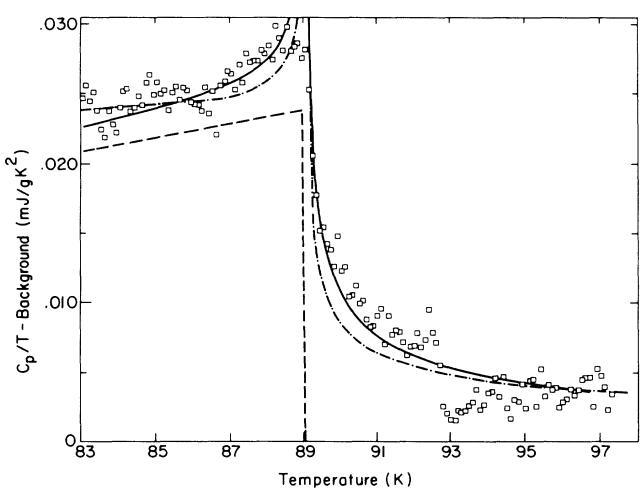

FIG. 2. The data of Fig. 1 with a sloping background subtracted. The dashed curve is the fitted BCS-type contribution and the solid curve, the sum of the BCS-type part and the $d=3$ Gaussian fluctuation contribution. The dash-dotted curve is the best fit for $d=2$ (different background included).

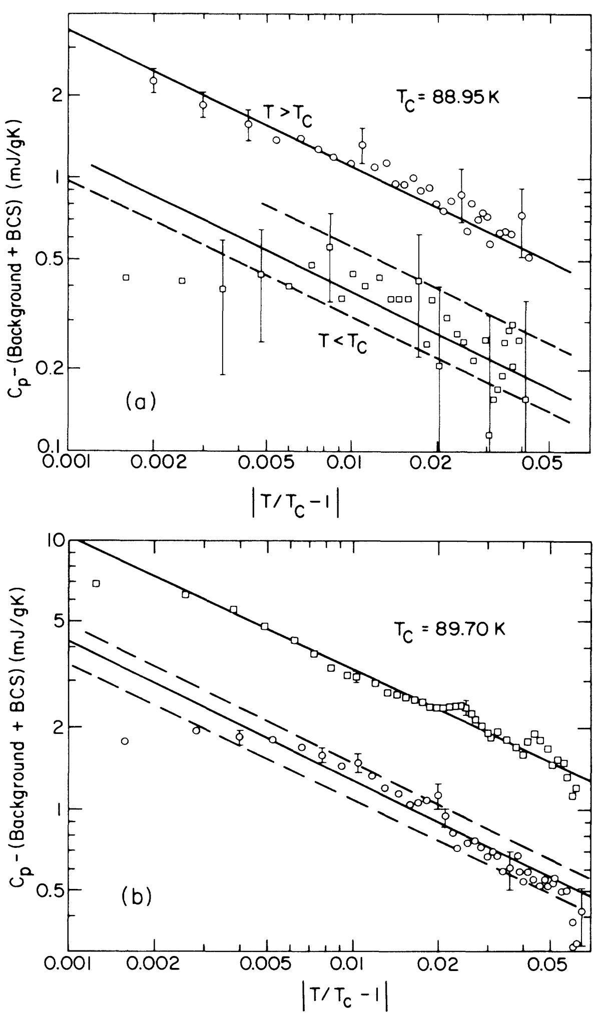

FIG. 3. (a) The logarithm of C_p of the Argonne crystal, after subtraction of both the background and BCS-type contributions, vs the logarithm of $|T/T_c - 1|$. The solid lines are the fits of Fig. 2. The dashed lines give the range of possible Gaussian amplitudes below T_c. (b) Similar analysis for the Illinois sample. Note the larger amplitude for this completely superconducting crystal.

plore further the possibility of 2D Gaussian fluctuations or critical phenomena, we have plotted the C_p data for both samples on a log-log plot in Fig. 3. In this case, both the linear background and the fitted BCS-type contribution (5) have been subtracted from the data. The data for $t > 0$ fit a power law over one and a half decades with an exponent of 0.5, clearly ruling out both an exponent of 1 (2D Gaussian fluctuations) and a logarithmic divergence, thereby fixing $d = 3$. As is evident in Fig. 3(a), the small signal-to-noise ratio for the $t < 0$ data renders a definitive analysis difficult. However, the data are consistent with a square-root power law with the amplitude ratio $C^+/C^- = 2.8 \pm 0.8$ $(5.6 \leq n \leq 10.2)$. The Illinois sample [Fig. 3(b)] gives $C^+/C^- = 2.5 \pm 0.3$ $(6.2 \leq n \leq 8)$. These results rule out a two-component order parameter. The Illinois sample, which is completely superconducting, shows some signs of a crossover to true critical behavior. An examination of that possibility will be treated in a subsequent publication.

In summary, we have observed bulk Gaussian thermodynamic fluctuations in crystals of $YBa_2Cu_3O_{7-\delta}$. It is important that specific-heat measurements are insensitive to small volume fractions of filaments and loops that can mimic paraconductivity and other precursive effects in an inhomogeneous material. This is the first observation of specific-heat fluctuations in a bulk superconductor, and adds strong evidence that the superconductivity of this class of material is three dimensional. The order parameter has more than two components.

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