Physica C 153-155 (1988) 1082-1085
North-Holland, Amsterdam

SPECIFIC HEAT OF A SINGLE CRYSTAL OF $YBa_2Cu_3O_{7-\delta}$: FLUCTUATION EFFECTS IN A BULK SUPERCONDUCTOR IN ZERO MAGNETIC FIELD AND IN A MAGNETIC FIELD

D. M. GINSBERG, S. E. INDERHEES, M. B. SALAMON, NIGEL GOLDENFELD, J. P. RICE, AND B. G. PAZOL

Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, 1110 W. Green St.; Urbana, IL 61801*

We have measured the specific heat of a single crystal of $YBa_2Cu_3O_{7-\delta}$. Thermodynamic fluctuations, evident in deviations of the data from a BCS-like step, are well described by 3-dimensional (3D) Gaussian fluctuations. The results imply that the number of components of the order parameter is 7 ± 2. When a magnetic field is applied parallel to the c axis, the specific heat peak broadens and decreases in amplitude, with little shift in position. The difference between the zero field specific heat and that measured in a field is found, however, to satisfy a scaling relation suggesting critical, rather than Gaussian, fluctuations.

1. INTRODUCTION

In the high-temperature superconductor $YBa_2Cu_3O_{7-\delta}$ the BCS coherence length ξ_0 is orders of magnitude smaller than in conventional superconductors, making it possible to study the effect of thermodynamic fluctuations in the neighborhood of T_c for bulk samples. The fluctuation of small regions of a sample into the superconducting state when T is just above T_c has been studied in polycrystalline samples by measurements of resistivity and susceptibility (1-3), and has been interpreted in terms of 3-dimensional (3D) Gaussian fluctuations of short-lived Cooper pairs. We report here the first observation of the specific heat anomaly in a single crystal of high temperature superconductor, and the first observation of the Gaussian-fluctuation contribution to the specific heat of a 3D superconducting transition.

2. SAMPLE PREPARATION

The crystal was made by a flux technique similar to that used in the pioneering work of Schneemeyer et al. (4). The starting materials were at least 99.999% pure. They were carefully weighed out without first contaminating them with water vapor, O_2 or CO_2, were thoroughly mixed and ground, and were then loosely poured into a crucible made of 10.5% yttria-stabilized zirconia. The material was heated by stages in air and cooled again We crushed the crucible in a hydraulic press, revealing a flat cavity that had formed in the matrix near the bottom of the crucible. Numerous crystals had broken away from the cavity walls, and were harvested. Other crystals were plucked gently from the cavity wall with tweezers. Laue backscattering x-ray diffraction showed that the c axis was perpendicular to the largest faces, and that the lattice constants had the expected values. To bring the oxygen stoichiometry to the desired value, the crystals were heated and then cooled in flowing oxygen on a wafer of polycrystalline $YBa_2Cu_3O_{7-\delta}$. (5). The transition occurs at approximately 90K; it is narrow and well shaped. (5)

3. EXPERIMENTAL METHODS

The crystal, with a mass of 620 μg, was mounted with a small amount of GE varnish on a thermocouple formed from thin, flattened Chromel and Alumel wires. We used a standard ac calorimetric method. The exposed (001) face was darkened with DAG colloidal graphite to enhance light absorption. One arm of the thermocouple detected the ac temperature oscillations induced by chopped-light heating; the second arm monitored the slight dc temperature offset of the sample from the thermal bath. The data were taken by increasing the sample temperature at a rate of about 0.1K/min.

4. ZERO-FIELD SPECIFIC HEAT DATA AND THEIR INTERPRETATION

In Fig. 1, C/T is plotted in the vicinity of the superconducting transition. Because the BCS coherence length ξ_0 of ordinary superconductors is large, mean-field theory is valid to extremely small values of $t = (T/T_c - 1)$, and the specific heat jump predicted by the BCS theory is observed for those materials.

*This research was supported by National Science Foundation grants DMR-85-01346 and DMR-86-12860. One of us (NG) gratefully acknowledges the support of an A. P. Sloan Fellowship.

0921-4534/88/$03.50

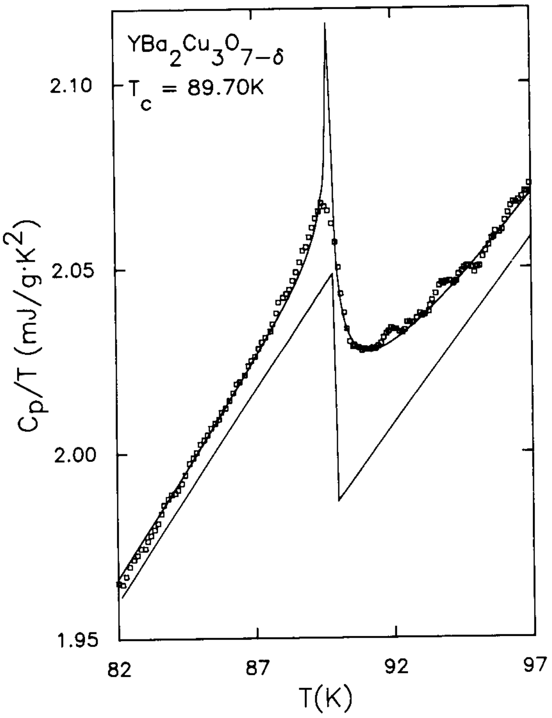

FIGURE 1
Specific heat of the sample in zero applied field. The step-like curve is the sum of the BCS-like and background contributions. The solid line is a fit to the sum of all the contributions.

Thouless (6) and then Aslamazov and Larkin (7) predicted that the specific heat has a Gaussian-fluctuation contribution in the mean field regime, given above (+) and below (-) T_c by

$$\Delta C = C_{\pm}|t|^{-1/2} \quad (1)$$

For quadratic (i.e., Gaussian) fluctuations about mean-field theory in a O(n) model, the amplitudes are in the ratio

$$C_+/C_- = n/2^{d/2} \quad (2)$$

where n is the number of components of the order parameter and d is the dimensionality. (8) In can be shown that electromagnetic interactions between fluctuations make a negligible correction to Eq.(2) for extreme type II superconductors. Note that even for the small Ginzburg-Landau coherence lengths expected (9) for $YBa_2Cu_3O_{7-\delta}$, the Ginzburg criterion for n=2,

$$|t| >> (1/32\pi^2)(k_B/\Delta C\xi_0{}^3)^2$$

predicts that critical effects (from interactions between fluctuations which should occur close to $|t|=0$) should not be observable for $|t|>10^{-3}$. In addition to the contribution of the Gaussian fluctuations to the specific heat, there is, presumably, the usual BCS contribution for $(-0.1\leq t\leq 0)$,

$$C_{BCS} = 1.43\gamma_{eff}(1 + 1.83t), \quad (3)$$

where the specific heat coefficient γ_{eff} includes possible strong-coupling corrections. Eq.(3) is a fit to Muhlschlegel's theoretical results. (10) The lattice contribution to the specific heat is approximated by a linear (in t) background. We treat the magnitude and slope of that background as well as C_+ and γ_{eff} as adjustable parameters, making no assumption that the mean-field discontinuity in the specific heat 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 looking at log-log plots of the data to be sure that the specific heat singularity is a power law with the same exponent above and below T_c. In Fig. 1 we have plotted the sum of all contributions as a curve through the data, using $C_+/C_- = 2.5$ and T_c = 89.7K. The step-like curve is the sum of the BCS-like and background contributions, showing clearly the fluctuation terms. The fit yields the value

$$C_+ = 2.0 \pm 0.1 \text{ mJ/cm}^3\text{K}. \quad (4)$$

This value of the amplitude corresponds to a Ginzburg-Landau coherence length of 7Å. Assuming a density of 6.4 g/cm^3, the fit of Fig. 1 gives a value

$$1.43\gamma_{eff}T_c = 36 \pm 2 \text{ mJ/cm}^3\text{K}, \quad (5)$$

which agrees well with our earlier value (11) of 40 ± 4 mJ/cm^{3}K for a polycrystalline sample.

To explore the possibility of 2D Gaussian fluctuations or critical phenomena, we plotted the specific heat data on a log-log plot in Fig. 2. We have subtracted from the data both the linear background and the fitted BCS-like contribution given in Eq.(3). For t>0 the data fit a power law over one and one half decades with an exponent of 0.5, clearly ruling out both an exponent of 1 (2D Gaussian fluctuations) and a logarithmic divergence. The dimensionality is evidently d = 3. For t<0 the signal-to-noise ratio is not as good, so a definitive analysis is impossible. The data are, however, consistent with a square-root power law with the amplitude ratio $C_+/C_- = 2.5 \pm 0.6$. From Eq.(2) we find

$$n = 7 \pm 2. \quad (6)$$

This result rules out the possibility of a two-component order parameter, as in the Landau-Ginzburg theory. The sample data show some signs of a crossover to true critical behavior.

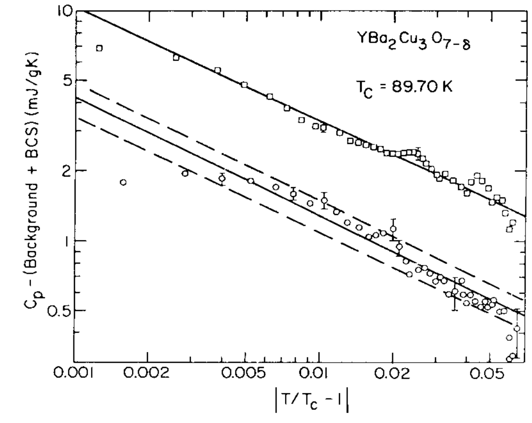

FIGURE 2
The specific heat, after subtraction of both the background and the BCS-like contributions, vs. $|T/T_c - 1|$ on a log-log plot. The solid lines show the fit of Fig. 1. The dashed lines give the range of possible Gaussian amplitudes below T_c.

5. EFFECT OF A MAGNETIC FIELD

In conventional superconductors, the main effect of a magnetic field is to shift the transition to a lower temperature, with little broadening of it. However, the resistive transition in $YBa_2Cu_3O_{7-\delta}$ is strongly broadened in a field, even for single crystal samples. (12) We find that the specific heat peak is also broadened.

Lee and Shenoy (13) calculated the field dependence of the excess specific heat C_H caused by Gaussian fluctuations in both the clean and dirty limits:

$$C_H = h^{-1/2}f(t_H/h) \qquad (7)$$

where $h=\xi^2(0)H/\phi_0$. $t_H=T/[T_c(H)-1]$, and ϕ_0 is the flux quantum. For x>>1, $f(x) \rightarrow x^{-1/2}$, leading to Eq.(1).

For the field-dependent measurements, sample rotation was carefully prevented. The temperature was measured with carbon-glass sensor, and the usual corrections for magnetic field effects were made. The field was applied in the c-axis direction above 100K, and the sample was cooled to about 75K in the field to guarantee field uniformity. The specific heat data were collected while the sample was heated.

Since no field dependence was detected at 77K, we normalized each run to the bulk specific heat of the polycrystalline material measured at 77K. To eliminate the large lattice background, we subtract the specific heat in a field from that in zero field at the same temperature; the result is plotted in Fig. 3. The results shown in Fig. 3 are qualitatively different from the behavior of other superconductors, where the shift of the specific heat anomaly to lower temperatures is larger, and the broadening less, than we see.

Lee and Shenoy demonstrated theoretically that the magnetic field broadens the width of the critical region significantly. We therefore perform a scaling analysis, assuming that the magnetic field enters into the singular part of the free energy through the term (p-2eA/c); A scales, therefore, as an inverse length. We then conclude that the fluctuation contribution to the free energy has a scaling form

$$F_{fl} = h^{d/2}g(t_H/h^{1/2\nu}) \qquad (8)$$

where ν is the exponent governing the divergence of the correlation length. The specific heat which one calculates from Eq.(8) is of the form

$$C_H = h^{(d/2-1/\nu)}g''(t_H/h^{1/2\nu}). \qquad (9)$$

The mean field result $\nu=1/2$ leads back to Eq.(7), as it must. If we measure C in zero field and in a field at temperatures which are equidistant from the critical point on a t plot, we can write

$$(C_0-C_H)h^{(1/\nu-d/2)} = f(t/h^{1/2\nu}), \qquad (10)$$

where f(x) is a scaling function. Only the part of the specific heat associated with the superconducting transition satisfies Eq.(10). To perform the subtraction at equal values of

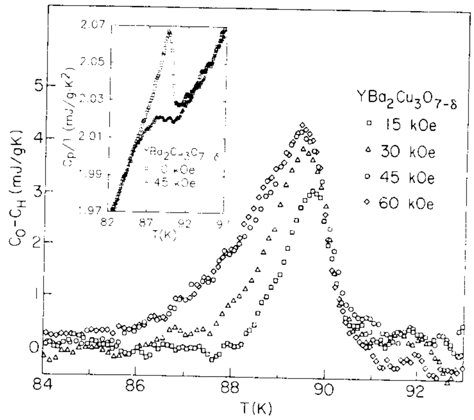

FIGURE 3
C_0-C_H vs temperature T at various fields. Inset: Zero-field and 45 kOe data from which difference data were extracted.

t, we would first have to remove the dominant lattice and normal electron background from each curve - a very imprecise procedure. Fortunately, the subtraction in Fig. 3 shows that the peak position shifts only by about 0.3K ($\delta t \approx 3 \times 10^{-3}$) over our field range, and this has negligible effect on the scaling which we discuss. Note in Fig. 3 that the peak increases with field. If we take the peak to be at t=0, Eq.(10) requires a negative power of h on the left hand side; i.e., $\nu > 2/d$. Indeed, the data can be collapsed onto a single curve by choosing a value $\nu = 0.75 \pm 0.03$, as shown in Fig. 4. Note that the d=3 Gaussian-fluctuation value $\nu = 1/2$ gives the wrong qualitative behavior, while both the d=3 critical behavior (14) ($\nu = 2/3$) and the d=2 Gaussian fluctuations ($\nu = 1$) predict no field dependence for $C_0 - C_H$ at t=0. The value $\nu = 0.75$ corresponds, in the O(n) model, to n≈6 (epsilon-expansion) or n≈4 (1/n expansion) in agreement with our conclusion from the zero-field data that n > 2.

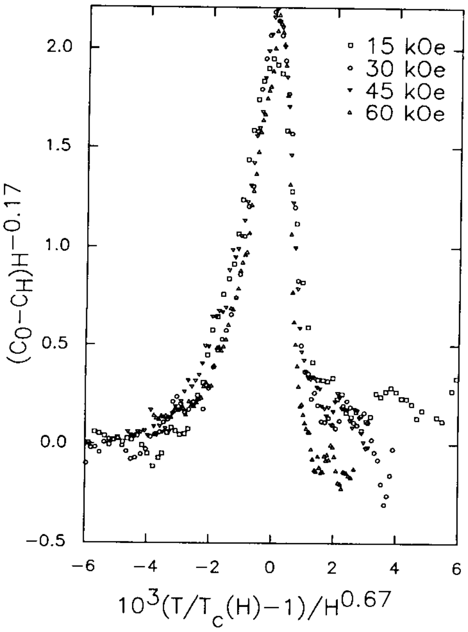

FIGURE 4
Scaling of the data of Fig. 4. The values of $T_c(H)$ used are: 89.7K at 15kOe; 89.6K at 30kOe; 89.5K at 45kOe; and 89.3K at 60kOe.

6. CONCLUSIONS

We have interpreted our data in zero field in terms of Gaussian fluctuations. An attempt to fit those data to critical behavior yields a far poorer fit. (15) On the other hand, the effect of an applied magnetic field is more indicative of critical behavior. These observations suggest that the magnetic field may expand the critical region of temperature.

Our specific heat measurements are being reported in more detail elsewhere. (16,17).

REFERENCES

(1) P. P. Freitas, C. C. Tsuei, and T. S. Plaskett, Phys. Rev. B36, 833 (1987).
(2) N. Goldenfeld, P. D. Olmsted, T. A. Friedmann, and D. M. Ginsberg, Solid State Commun., in print.
(3) M. Dubson, J. J. Calabrese, S. T. Herbert, D. C. Harris, B. R. Patton, and J. C. Garland, in: Novel Superconductivity, eds. S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987) pp. 981-982.
(4) L. F. Schneemeyer, J. V. Waszczak, T. Siegrist, R. B. van Dover, L. W. Rupp, B. Batlogg, R. J. Cava, and D. W. Murphy, Nature 328, 601 (1987).
(5) J. P. Rice, B. G. Pazol, D. M. Ginsberg, and M. B. Weissman, in print.
(6) D. J. Thouless, Ann. Phys. 10, 553 (1960).
(7) L. G. Aslamazov and A. I. Larkin, Sov. Phys. Sol. St. 10, 875 (1968) [Fiz. Tverd. Tela 10, 1104 (1968).
(8) S.-K. Ma, Modern Theory of Critical Phenomena (Benjamin, New York, 1976), pp. 82-93. We have corrected Eq.(3.59).
(9) J. Bardeen, D. M. Ginsberg, and M. B. Salamon, in: Novel Superconductivity, ed. S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987) pp. 333-339.
(10) B. Muhlschlegel, Z. Phys. 155, 313 (1959).
(11) S. E. Inderhees, M. B. Salamon, T. A. Friedmann, and D. M. Ginsberg, Phys. Rev. B36, 2401 (1987).
(12) T. K. Worthington, W. J. Gallagher, and T. R. Dinger, Phys. Rev. Lett. 59, 1160 (1987).
(13) P. A. Lee and S. R. Shenoy, Phys. Rev. Lett. 28, 1025 (1972).
(14) C. J. Lobb, Phys. Rev. B36, 3930 (1987).
(15) M. B. Salamon, S. E. Inderhees, J. P. Rice, B. G. Pazol, D. M. Ginsberg, and N. Goldenfeld, Phys. Rev., in print.
(16) S. E. Inderhees, M. B. Salamon, N. Goldenfeld, J. P. Rice, and D. M. Ginsberg, Phys. Rev. Lett., in print.
(17) M. B. Salamon, S. E. Inderhees, J. P. Rice, B. G. Pazol, D. M. Ginsberg, and N. Goldenfeld, Phys. Rev., in print.