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# Heat-capacity studies of reduced-oxygen-content $YBa_2Cu_3O_{7-x}$ near the superconducting transition

K. Ghiron and M. B. Salamon
*Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 60439*

B. W. Veal, A. P. Paulikas, and J. W. Downey
*Argonne National Laboratory, Argonne, Illinois 60439*
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We have performed high-resolution ac calorimetry near the superconducting transition of single crystals of reduced-oxygen-content $YBa_2Cu_3O_{7-x}$. The heat-capacity anomaly decreases dramatically with $T_c(x)$ despite the fact that the transition width and the Meissner fraction indicate that the samples are of similar quality. In addition, the sensitivity of the heat-capacity anomaly to magnetic fields is several times stronger in these samples than has been observed in previous work on fully oxygenated samples. The reduction in the amplitude of the heat-capacity anomaly corresponds to the reduction in the apparent density of states at the Fermi surface.

Reduced-oxygen-content $YBa_2Cu_3O_{7-x}$ has several unusual properties. Optical, NMR, and neutron-scattering data reveal the persistence of a gaplike feature above the transition temperature in lower-$T_c$ samples.[1-5] The slope change at $T_c(x)$ in the NMR $T_1$ data for planar copper sites is reduced as oxygen is removed.[6] Resistivity measurements indicate a decrease in the pinning energy near the transition temperature in only slightly oxygen-deficient single crystals.[7] Heat-capacity measurements by Salasky *et al.*,[8] Junod and co-workers,[9-11] and Wühl *et al.*[12] have demonstrated that the heat-capacity jump size is strongly dependent on the oxygen content. Magnetization measurements have also been used to demonstrate that the size of the heat-capacity jump should decrease with oxygen depletion.[13] Despite all this work the nature of the changes induced by removing oxygen remains unclear.

Here we report the direct measurement of the heat capacity of single-crystal samples with transition temperatures as low as 60 K. The heat-capacity anomaly becomes smaller and broader as oxygen is removed. A 10% reduction in the transition temperature results in a fivefold reduction in $\Delta C_{max}$, the maximum difference between the heat capacity and the extrapolated normal-state background. The amplitude appears to decrease approximately as $1/[T_c(0)-T_c(x)]$. The decrease in the amplitude follows changes in the apparent density of states at the Fermi surface as measured by the Knight shift of planar copper nuclei. The increasing anisotropy and fluctuation effects as well as similarities with other two-dimensional superconductors suggest that the reduced anomaly is caused by the transition becoming more two-dimensional.[14,15]

The samples were prepared at Argonne National Laboratories by a method published elsewhere.[16] These samples exhibit 10–90% transition widths less than 2.5 K for all degrees of oxygen reduction as determined by magnetization measurements in a 0.5-Oe field. The Meissner fraction and transition widths do not depend systematically on the transition temperature. All of the samples contain 3 at. % of gold impurities because the samples were prepared using gold crucibles. Data on fully-oxygenated samples with no gold impurities have heat-capacity anomalies 20–40% larger than fully oxygenated samples with gold impurities. The gold impurities which preferentially occupy sites in the CuO chains only slightly increase the transition temperature.[17] The samples with a transition temperature of 86 and 60 K were mechanically thinned, while the other crystals were not modified after their growth and oxygenation.

The heat capacity was measured by the same ac method as used by Inderhees *et al.*[18] The heat input is supplied by chopped light absorbed by a thin coating of colloidal graphite. Because the amount of light absorbed is unknown all the samples are assigned the same heat capacity at 100 K despite the changing oxygen content. This leads to a systematic error in the estimation of $\Delta C_{max}$ for samples with lower transition temperatures. The heat capacity at 100 K in J/(mol K) changes by less than 5% as $x$ is increased from 0.0 to 0.2 and thus the systematic error due to the normalization is also less than 5%.[11]

The results are shown in Fig. 1. The most striking feature is that the size of the peak is rapidly reduced as the transition temperature is lowered. The heat-capacity anomaly remains well defined and the shape of the peak becomes broader. Runs on samples with transition temperatures less than 70 K usually show only a slope change and no sign of a jump or a peak. One sample with $T_c=60$ K, which was quenched to nitrogen temperatures and measured without allowing the sample to warm for more than 1.5 h, did show a small peak with an amplitude of about 0.45 mJ $g^{-1}K^{-1}$. The quenching procedure may prevent any ordering of the oxygen atoms.

 

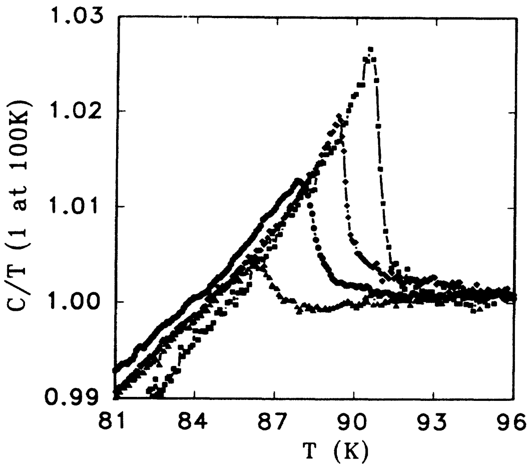


FIG. 1. Heat capacity (per unit volume) divided by the temperature. The value of $C/T$ has been set to be 1 at 100 K for all the samples.

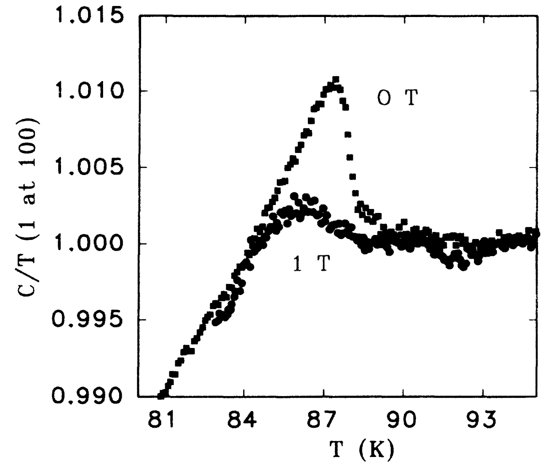


FIG. 3. The heat capacity (per unit volume) divided by the temperature is plotted for a sample with an 88-K transition temperature in zero and 1-T fields. The reduction of the heat-capacity anomaly in a 1-T field is substantially larger in this sample than has been observed in fully oxygenated samples before.

This 60-K sample was mechanically thinned for the experiment. In Fig. 2, we plot the amplitude of the anomaly $\Delta C_{max}$, the maximum difference between the heat capacity and the extrapolated normal-state background, as a function of $1/(93\text{ K}-T_c)$. The linearity of the result demonstrates the tendency for the peak amplitude to diverge as $1/(93\text{ K}-T_c)^{1\pm0.5}$.

The field dependence of the heat-capacity anomaly of a sample with a transition temperature of 88 K is shown in Fig. 3. The effect of the field on the heat-capacity jump is about 5–6 times stronger than in fully oxygenated samples without gold impurities. In other words, the amplitude of the anomaly is reduced in a 1-T field as much as the amplitude of the anomaly of a fully oxygenated sample is reduced in a 5–6-T field. The heat capacity is sensitive to the presence of a 1-T magnetic field, in the 88-K gold-doped sample, over a temperature range about 0.5° wider than in fully oxygenated samples without gold impurities. A strong reduction in the effective $H_{c2}(0)$ was also noted by Welp *et al.*[19]

In weak-coupling BCS theory the heat-capacity jump is proportional to $T_cN(0)$, where $N(0)$ is the density of states at the Fermi surface. An approximate equation for the transition temperature for all coupling strengths is that

$$T_c=0.25\tilde{a}\{\exp[2/N(0)V]-1\}^{-1/2}, \quad (1)$$

where $V$ is the strength of the attractive interaction, and $\tilde{a}$ is a temperature defined by an average over the coupling function.[2,0] Knight-shift measurements on the planar copper sites indicate that the apparent density of states at the Fermi energy at the transition temperature is about 4–10 times smaller in 60-K crystals than in 90-K crystals.[21,22] Including the factor of $\frac{2}{3}$ change in the transition temperature, this suggests that the heat-capacity anomaly should be about 6–15 times smaller in 60-K crystals than in 90-K crystals as we have observed. If the density of states at the Fermi surface changes by such a large factor, then one must assume that $V$ increases by a similar factor, if the transition temperature is to be given by Eq. (1). $^{17}$O NMR relaxation measurements in cuprate superconductors by Reven *et al.* were inconsistent with strong-coupling corrections.[23] Thus the rapid reduction of the Knight shift and the reduced entropy change at the transition cannot be explained by simple Fermi-liquid arguments even when strong-coupling corrections are included.

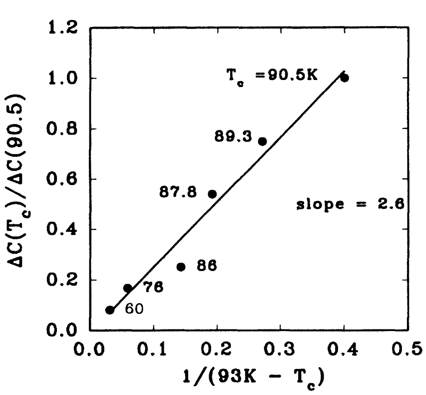


FIG. 2. This illustrates that the amplitude of the heat-capacity anomaly decreases as $1/(93\text{ K}-T_c)$ and thus tends to diverge as the samples become fully oxygenated.

We now consider mechanisms that might cause the observed reduction in $\Delta C_{max}$. The simplest is that the superconducting fraction is reduced as oxygen is removed. However, magnetization measurements indicate that the Meissner fraction and transition widths of these samples are similar with the exception of the mechanically thinned sample ($T_c=86$ K) (Fig. 4). In the absence of flux pinning the Meissner fraction indicates the fraction of the sample which is superconducting. In addition, the shielding fraction of a single sample which was reoxygenated did not show any dependence on the transition temperature. Finally, the large increase in the sensitivity

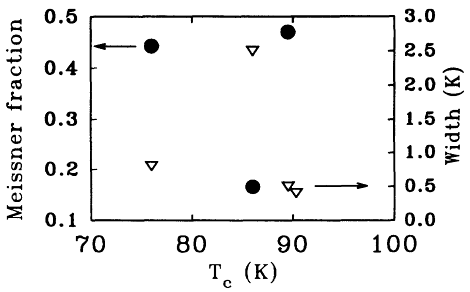


FIG. 4. The Meissner fraction and transition width as a function of the transition temperature for some of the samples on which the heat-capacity measurements were made.

of the heat-capacity anomaly to magnetic fields indicates a fundamental change in the transition which cannot be explained by a simple reduction of the superconducting fraction. Thus it is apparent that problems with sample quality are not the cause for the rapid reduction of the heat-capacity anomaly.

Another possible explanation is that the fast reduction of the amplitude of the heat-capacity anomaly occurs because of increased scattering. However, calculations by Abrikosov and Gorkov indicate such a fast reduction of the amplitude cannot result from impurity scattering,[24] even accounting for a strong-coupling enhanced gap. NMR measurements by Dupree indicate that chain doping affects the transition through changes in the density of states at the Fermi surface and not through scattering effects.[25] Also one would not expect a transition which is suppressed by scattering to show signs of a persistent gap above the transition temperature. Furthermore, Uemura *et al.* have observed a relationship between the penetration depth and the transition temperature which is inconsistent with scattering effects.[26,27] It seems unlikely that the dramatic reduction of the amplitude of the heat-capacity anomaly occurs because of the effects of scattering, magnetic or resonant.

Because of the short coherence length and the persistence of gaplike features above the transition temperature, it has been suggested that Cooper pairs form above the transition temperature. However, the in-plane coherence length actually increases with decreasing transition temperature[19] and the $c$-axis coherence length cannot decrease. In addition, the Bose condensation temperature remains well above the superconducting transition temperature as oxygen is removed.[26] Thus a crossover to a three-dimensional (3D) Bose condensation is also an unlikely cause for the observed reduction of the heat-capacity anomaly.

A crossover to a two-dimensional transition is suggested by the observation that the anisotropy increases as oxygen is removed from 1:2:3 samples.[14,15,28,29] In addition, a two-dimensional superconducting transition should only show a broad maximum in the heat capacity centered at a temperature above the superconducting transition with at most a small sharp feature at the transition temperature.[30] Thus as a system becomes more two-dimensional the size of the heat-capacity anomaly at the superconducting transition temperature should be reduced as we have observed. Even fully oxygenated bulk samples have shown temperature-dependent resistivities which are consistent with a Kosterlitz-Thouless–like transition.[31,32] Monte Carlo simulations[33] have demonstrated in an analogous spin system that the heat-capacity anomaly at the transition temperature disappears when the $c$-axis coupling is reduced below about 20–40% of the in-plane coupling. Because even in fully oxygenated Y-Ba-Cu-O the $c$-axis coupling is 12–25% of the in-plane coupling, our results are consistent with these simulations even though a simulation of an anisotropic superconductor should include Josephson couplings.

Adding weight to a 2D interpretation is the demonstration by Uemura *et al.* that the transition temperatures of a wide variety of high-temperature superconductors are proportional to the ratio of the two-dimensional density of superconducting carriers to the effective mass.[26] Previously, Nelson and Kosterlitz demonstrated that the Kosterlitz-Thouless transition temperature in a neutral superfluid is $h^2 n_B d/(8\pi k_B m^*)$, which is also proportional to the same ratio; $n_B$ is the density of superconducting bosons or Cooper pairs.[34] This transition temperature is in better agreement with Uemura's results than is the three-dimensional Bose transition temperature. In a two-dimensional system fluctuations are enhanced, thus the heat capacity should be more sensitive to the presence of a magnetic field.

Other highly anisotropic low-$T_c$ superconductors have properties similar to the high-temperature superconductors. $TaS_2$, which is more anisotropic than fully oxygenated Y-Ba-Cu-O, also has a heat-capacity anomaly whose amplitude is very sensitive to the transition temperature for different intercalations.[35] In addition $TaS_2(Py)_{1/2}$ like $YBa_2Cu_3O_{7-x}$ shows a highly anisotropic increase in diamagnetism at temperatures many times that of the superconducting transition temperature.[36] In $TaS_2(Py)_{1/2}$ the temperature dependence of the diamagnetic down turn is also consistent with two-dimensional fluctuations. The down turn has sometimes been attributed to the presence of the formation of a charge-density wave (CDW) in the unintercalated compound, but the intercalated compound does not undergo a CDW transition.[37] These similarities between the high-temperature cuprate superconductors and the intercalated low-temperature superconductors, which have more traditional Fermi-liquid-like normal-state properties, suggest that our observations are caused by phenomena associated with the dimensionality of the materials and not by phenomena that are unique to the cuprate superconductors.

We have observed a rapid reduction in the size of the heat-capacity anomaly in reduced-oxygen $YBa_2Cu_3O_{7-x}$. This reduction appears to be an intrinsic property of the crystals. The reduction is also correlated to the reduction of the apparent density of states as determined by the copper Knight shift in reduced-oxygen-content materials at the transition temperature. Comparisons with intercalated $TaS_2$ suggest that the reduction in the density of states at the Fermi surface may be characteristic of two-dimensional superconducting materials. However, we cannot determine whether the reduction in the apparent density of states and the corresponding reduction in the entropy change at the transition are caused by superconducting fluctuations or by the formation of some type of spin order.

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[1]W. W. Warren, Jr., *et al.*, Phys. Rev. Lett. **62**, 1193 (1989).

[2]S. L. Cooper *et al.*, Phys. Rev. B **40**, 11 358 (1989).

[3]F. Slakey, Phys. Rev. B **42**, 2643 (1990).

[4]J. Orenstein *et al.*, Phys. Rev. B **42**, 6342 (1990).

[5]J. Rossat-Mignod *et al.*, Physica B **169**, 58 (1991).

[6]T. Imai, Physica C **162-164**, 169 (1989).

[7]R. B. van Dover, L. F. Schneemeyer, R. J. Felder, and J. V. Waszczak, Physica C **193**, 13 (1992).

[8]M. Salaski *et al.*, Physica C **162-164**, 103 (1989).

[9]A. Junod *et al.*, Physica C **162-164**, 1401 (1989).

[10]A. Junod *et al.*, Physica C **162-164**, 482 (1989).

[11]A. Junod *et al.*, *Physical Properties of High Temperature Superconductors II*, edited by D. M. Ginsberg (World Scientific, Teaneck, NJ, 1990).

[12]H. Wühl *et al.*, Physica C **185-189**, 755 (1991).

[13]Manfred Däumling, Physica C **183**, 293 (1991).

[14]C. Marin, Physica C **185**, 1867 (1991).

[15]Kazushi Kanoda, J. Phys. Soc. Jpn. **57**, 1554 (1988).

[16]B. W. Veal *et al.*, Phys. Rev. B **42**, 6305 (1990).

[17]M. Z. Cieplak *et al.*, Phys. Rev. B **42**, 6200 (1990).

[18]S. E. Inderhees *et al.*, Phys. Rev. Lett. **60**, 1178 (1988); M. B. Salamon *et al.*, Phys. Rev. B **38**, 885 (1988).

[19]U. Welp *et al.*, *Physical Phenomena at High Fields,* edited by E. Manousakis (Addison-Wesley, Reading, MA, 1991), p. 403.

[20]V. Z. Kresin, Phys. Lett. A **122**, 434 (1987).

[21]R. E. Walstedt *et al.*, Phys. Rev. B **41**, 9574 (1990).

[22]M. Takigawa *et al.*, Phys. Rev. B **43**, 247 (1991).

[23]L. Reven *et al.*, Phys. Rev. B **43**, 10 466 (1991).

[24]K. Maki, *Superconductivity,* edited by R. D. Parks (Marcel Dekker, New York, 1969), p. 1035.

[25]R. Dupree, A. Gencten, and D. McK. Paul, Physica C **193**, 81 (1992).

[26]Y. J. Uemura *et al.*, Phys. Rev. Lett. **62**, 2317 (1989); **66**, 2665 (1991).

[27]J. W. Thomasson and D. M. Ginsberg, Phys. Rev. B **15**, 4270 (1977).

[28]K. E. Gray *et al.*, Phys. Rev. B **45**, 10 071 (1992).

[29]D. A. Brawner, Z. Z. Wang, and N. P. Ong, Phys. Rev. B **40**, 9329 (1989).

[30]D. Finotello *et al.*, Phys. Rev. Lett. **61**, 1954 (1988).

[31]P. C. Stamp *et al.*, Phys. Rev. B **38**, 2847 (1988).

[32]N. C. Yeh and C. C. Tsuei, Phys. Rev. B **39**, 9708 (1989).

[33]Wolfhard Janke and Tetsuko Matsui, Phys. Rev. B **42**, 10 673 (1990).

[34]D. R. Nelson and J. M. Kosterlitz, Phys. Rev. Lett. **39**, 1201 (1977).

[35]F. J. DiSalvo *et al.*, Phys. Rev. Lett. **27**, 310 (1971).

[36]T. H. Geballe, A. Menth, F. J. DiSalvo, and F. R. Gamble, Phys. Rev. Lett. **27**, 314 (1971).

[37]R. H. Friend and A. D. Yoffe, Adv. Phys. **36**, 1 (1987).