RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 37, NUMBER 7 1 MARCH 1988

Low-temperature specific heat of single-crystal $YBa_2Cu_3O_{7-\delta}$

S. von Molnár, A. Torressen, D. Kaiser, F. Holtzberg, and T. Penney
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598
(Received 3 November 1987)

The low-temperature specific heat has been measured on both orthorhombic (superconducting) and tetragonal single crystals of $YBa_2Cu_3O_{7-\delta}$. The Debye temperature extracted from the T^3 term decreases with increasing oxygen vacancy concentration consistent with glassy behavior in disordered solids. A linear γT term, however, exists for both phases. It is proposed that this term is at least in part electronic, even in the superconducting state, and is due to extended or localized states at the Fermi energy.

Although several workers have studied the low-temperature specific heat of ceramic forms of the $YBa_2Cu_3O_{7-\delta}$ (1:2:3) high-T_c superconductors,[1-4] to the best of our knowledge there exist no published data on single crystals of these materials.[5] From the data collected so far, it is clear that a low-temperature linear contribution is found in all cases. This fact is evidence against simple theories for superconductivity, in which an energy gap exists for all directions of k space. Alternatively, it may be the consequence of coexisting, noninteracting, superconducting, and normal bands. This paper presents low-temperature specific-heat measurements between approximately 2 and 10 K on a mosaic of 21 small single crystals[6] of (1:2:3) having a total mass of about 1 mg. Measurements were carried out both in the orthorhombic superconducting state ($0 < \delta < 0.3$) and in the tetragonal insulating state ($0.6 \lesssim \delta \lesssim 0.8$) (Ref. 7) accomplished by heating the sample at 600 °C for a total of 120 h in a vacuum of 7×10^{-7} Torr. Comparison of the specific-heat measurements on the same single crystals addresses the effects due to oxygen concentration.

The results presented in this paper demonstrate that the specific heat has a large linear term both in the superconducting ($\gamma\sim9$ mJ/molK^2) and insulating forms ($5 \leq \gamma \leq 9$ mJ/molK^2) of (1:2:3). Furthermore, the Debye temperature Θ, extracted from the cubic term, decreases in the tetragonal phase implying a softening of the phonons in this more disordered state.

The specific heat was measured using a thermal relaxation technique, first described by Forgan and Nedjat,[8] which gives valid results as long as the thermal diffusion times characteristic of the sample and between sample and bolometer are short compared to the measured relaxation times. To test the accuracy of the technique a 1.8 mg Cu sample, whose specific heat per gram at low temperature is comparable to that of the superconductor, was measured between 1.8 and 13 K. A three-parameter fit of the form $C = A_1T + A_2T^3 + A_3T^5$ yields the following values for A_i, with C in J/molK: $A_1 = 6.43\times10^{-4}(7.6)$, $A_2 = 5.75\times10^{-5}(20)$, and $A_3 = -9.86\times10^{-2}(22)$, where the number in parentheses is the percentage deviation from Ahler's results.[9] With $A_1 = \gamma$ and $A_2 = 1944r/\Theta^3$, where r is the number of atoms/molecule, we therefore estimate the error in this microcalorimetric measurement to be of order $\pm 15\%$ for both γ and Θ, the two quantities of interest for this paper. It should be noted that superconductors, with their inherent low thermal conductivity, K, are normally difficult to measure with this dynamic technique.[10] In the present experiment, however, these difficulties are alleviated in part by an anomalous contribution to K,[11] as well as the small mass of the individual crystals. Furthermore, the platelet morphology[6] maximizes coupling between sample and bolometer.

The crystal mosaic was either mounted directly on a commercial RuO_2 thick film resistor[12] with N grease, or onto a 7.6×10^{-3}-cm-thick single-crystal sapphire chip which was then placed on the bolometer. Since the experiment requires the subtraction of a background run from the data including the sample, these mounting procedures yield two independent measurements of the sample and afford an internal consistency check for the results.

The specific heat C of (1:2:3) plotted in the form C/T vs T^2 in both the oxygenated and vacuum annealed state is shown in Fig. 1. The lines through the three curves are polynomial fits of the form $C/T = A_1 + A_2T^2 + A_3T^4$, with the values given in Table I where C is the J/molK.

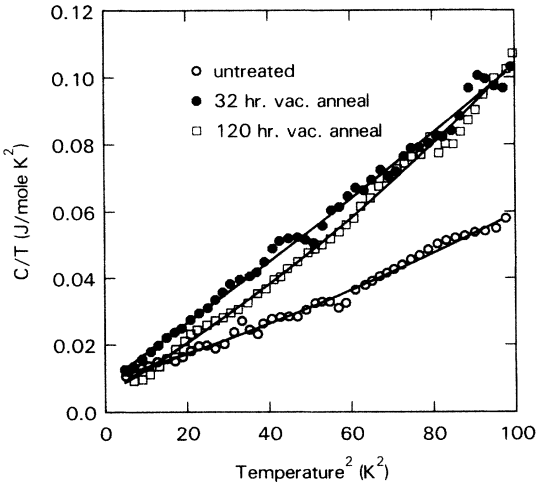

FIG. 1. Molar specific heat of $YBa_2Cu_3O_{7-\delta}$ divided by temperature as a function of temperature squared. The three curves represent the original single-crystal mosaic and the tetragonal form after two stages of vacuum anneal.

TABLE I. Properties of single-crystal $YBa_2Cu_3O_{7-\delta}$. A_i are the coefficients of polynomial fits of the form $C/T = A_1 + A_2T^2 + A_3T^4$ through the data of Fig. 1, with C in J/mol K.

Structure	Mass (mg)	δ	$A_1 = \gamma$	$A_2 \propto \Theta^{-3}$	A_3	T_c (K)
Orthorhombic	1.5	$0 < \delta \lesssim 0.3$	0.009	37×10^{-5}	1.3×10^{-6}	89
Tetragonal (32 h vac. anneal)	1.1	$0.6 < \delta \lesssim 0.8$	0.009	87×10^{-5}	7.6×10^{-7}	<2
Tetragonal (120 h vac. anneal)	1.0	$0.6 \lesssim \delta \lesssim 0.8$	0.005	71×10^{-5}	2.8×10^{-6}	<2

The most striking observation is the presence of a large linear term in both the orthorhombic and tetragonal phases. $\gamma = 9$ mJ/mol K^2, does not change, within the accuracy of this experiment, between the virgin and the initial vacuum annealed state, and remains large, 5 mJ/mol K^2, even after a total annealing time of 120 h. The absolute accuracy of the measurements for the annealed sample is considerably poorer than $\pm 15\%$, because one-third of the mass was lost in the processing steps. It should also be noted that the slope A_2 increases dramatically, implying a change in Θ from 410 to 300 K, well outside the range of the estimated error. The data for the superconducting orthorhombic sample may be compared to the ceramic data of Phillips *et al.*[1] who obtain $C/T = 0.0071 + 0.00032T^2 + 0.8\times10^{-6}T^4$ and who estimate $\Theta = 430$ K. Our value is also in good agreement with the estimates of Inderhees, Salamon, Friedmann, and Ginsberg[13] of $\Theta \approx 440$ K. This lends further credence to our measurements technique, since the lattice term is not expected to vary substantially between single crystals and ceramics.

To determine the effect of the vacuum anneal on the superconducting properties the magnetic susceptibility was measured in both phases. Figure 2 summarizes the results, all measured in an applied field of $H = 14$ Oe. Curve 1 represents the zero-field-cooled susceptibility which measures, below the transition temperature $T_c \sim 89$ K, the diamagnetic shielding of the superconductor. The apparent steps and broadness of the transition is attributed to a spread in oxygen concentration of the crystals in the mosaic. Curve 2 is the field-cooled susceptibility and measures the Meissner effect (flux exclusion) in the superconductor, approximately a 10% effect, most likely due to flux pinning sites of unknown origin. Curve 3 shows the zero-field-cooled susceptibility of the vacuum-annealed sample. It is seen that the signal has been reduced by about two orders of magnitude and that no obvious diamagnetic transition can be determined from the data. Apparently the material has been converted to the normal state. Although the crystals were too small to attempt transport measurements, equivalent vacuum annealing of ceramic material indicates that the material is an insulator.[14] Single-crystal x-ray measurements performed on one single crystal from each of the phases completed the characterization. The orthorhombic superconductor lattice constants, in angstroms, are $a = 3.819(2)$, $b = 3.891(2)$, $c = 11.746(4)$ whereas in the tetragonal form $a = b = 3.853(2)$ and $c = 11.868(4)$.

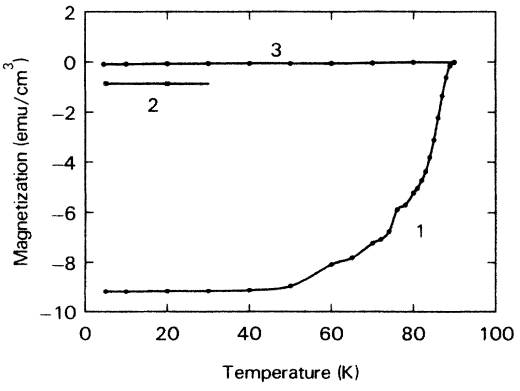

FIG. 2. Magnetization of $YBa_2Cu_3O_{7-\delta}$ as a function of temperature in an applied field $H = 14$ Oe. Curve 1 is zero-field cooled, curve 2 the field-cooled data for the orthorhombic mosaic. Curve 3 is the zero-field-cooled data for the tetragonal phase.

It is tempting to discuss the specific-heat results as arising from glassy behavior. As Jorgensen *et al.*[15] have shown, the oxygens order along the b axis chains with a fractional occupancy close to 1 in the nearly square planar $Cu\text{-}O_{4-x}$ units of the orthorhombic structure. In the tetragonal phase for $\delta \sim 0.5$, however, the fractional occupancy of the oxygen sites is 0.25 along the equivalent a and b axes leading to a highly disordered two-dimensional Cu-O network. The observed softening of the lattice (small Θ) is consistent with this idea and has been documented in many crystalline solids containing defects.[16] The decrease in the linear term, however, has an upper limit of order 50%, and it must be concluded that a large density of low-energy excitations (constant in energy) exists in both phases. Although disorder may contribute to the value $\gamma \simeq 9$ mJ/mol K$^2 \equiv 87\times10^{-6}$ J/cm^3 K^2, it is unlikely to explain the effect since γ is expected to increase in the tetragonal phase. Furthermore, values for typical insulating glasses, such as vitreous silica ($\gamma \sim 1\times10^{-6}$ J/cm^{3}K^2) and alumina ($\gamma \sim 10\times10^{-6}$ J/cm^{3}K^2) (Ref. 17) as well as amorphous superconductors such as $Zr_{0.7}Pd_{0.3}$ ($\gamma \sim 8\times10^{-6}$ J/cm^{3}K^2) (Ref. 18) are between one and two orders of magnitude smaller. Nor can the γ be explained in terms of twinning in the orthorhombic phase, since it is also present in the tetragonal form of the compound. We have recently become aware of antiferromagnetic order in the insulating phase of (1:2:3) (Ref.

19). This would, however, normally not lead to a linear term in the specific heat.[20] The possibility of two phases, i.e., a superconductive skin covering a normal or insulating crystal, is also unlikely. First of all, x-ray analysis of single crystals using Cu radiation, which probes at least 8 μm into the surface, yields an upper limit for the internal variation in $\delta = \pm 0.06$. Second, optical inspection of the orthorhombic phase indicates that the domain structure in the *a-b* plane is continuous throughout the crystal. Furthermore, the low-temperature upturn in $C(T)/T$ vs T^2 found in ceramic samples was not observed in our crystals down to approximately 2 K indicating that any presence of second phase is small.[4,11,21]

Based on the foregoing discussion, we suggest that most of the γ term is electronic in origin. For a conventional superconducting state this assignment requires some gapless regions on the Fermi surface. The origin of the gapless regions is either due to non-*S*-state pairing or the existence of more than one band at the Fermi energy E_F. We are aware of the evidence against the former from muon spin-relaxation (μSR) data[22] and several reports of leakage-free tunnel characteristics. It is clear, however, that all known single-crystal and ceramic experiments on these[1-4] and La-based oxides[23] as well as on the $BaPb_{1-x}Bi_xO_3$ superconductors[24] show comparable γ values, suggesting a common origin. The fact that γ does not change appreciably in going from the conducting to the insulating state can be accounted for with an all electronic model. The specific heat of Si:P near the metal-insulator phase transition varies only very weakly compared to the conductivity, and shows a well-defined linear term in the insulating state.[25] Furthermore, large γT terms in nonstoichiometric vanadium bronzes, which are hopping conductors, are well established.[26] Finally, variable range hopping transport of the form $\exp[(T_0/T)^{1/4}]$ has been observed in nonmetallic ceramic and single-crystal forms of nonstoichiometric La_2CuO_4.[27,28] All these results may be explained by a density-of-states picture analogous to that proposed for $Gd_{3-x}v_xS_4$,[29] a Th_3P_4-type structure containing vacancies v in which the carrier concentration is increased by filling of v by Gd atoms. Basically, the material becomes conducting when the Fermi energy E_F crosses a mobility edge E_μ, established by the random potentials created by v. We propose that defects (e.g., on the rare-earth site) and the oxygen vacancies inherent in both the orthorhombic and tetragonal structures[15] play a similar role. A nonvanishing density of electronic states at E_F, either localized ($E_F - E_\mu < 0$) or extended ($E_F - E_\mu > 0$) is a natural consequence of this picture. Of course in the limit of $\delta = 1$, the ordered state, this model does not apply. It is also possible that the finite γ may indicate unconventional superconductivity. For example, in the resonant valence bond model, in addition to the superconducting bosons, there are gapless uncharged fermions which yield a γ term.[30]

In summary, the low-temperature specific heat of single crystals $YBa_2Cu_3O_{7-\delta}$ in the orthorhombic, superconducting, and tetragonal state has been measured. The slope of the T^3 term increases with oxygen disorder consistent with a softening of the phonon spectrum in glassy materials. The γT term, however, remains finite and large. It is proposed that this term is at least in part electronic in origin, even in the superconducting state, and is due to states at the Fermi energy.

Note added in proof. A γ of about 4 mJ/mol K^2 has been observed for ceramic samples of $La_{1-x}Ba_xCuO_4$ in the superconducting phase for $x > 0.05$ and for a nonsuperconducting sample at $x = 0.04$. For $x < 0.025$ the samples are antiferromagnetic and no γ is observed.[31] The implication of this work is that the finite γ is intrinsic. The rapid change in γ from zero to a finite nearly constant value is inconsistent with either a two-level system or impurities.

We are grateful for illuminating discussion with Z. Fisk, R. G. Goodrich, P. Horn, R. Koch, P. A. Lee, and especially D. H. Lee for his critical reading of the manuscript. We particularly wish to thank J. O. Willis and Z. Fisk for availing us of their results prior to publication. The structural measurements of both phases by D. Keane and P. Horn are gratefully acknowledged as are the susceptibility measurements by T. R. McGuire and H. Lilienthal.

[1] N. E. Phillips, R. A. Fisher, S. E. Lacy, C. Marcenat, J. A. Olsen, W. K. Ham, A. M. Stacy, J. E. Gordon, and M. L. Tan, in *Proceedings of the Eighteenth Yamada Conference on Superconductivity in Highly Correlated Fermion Systems, Sendai, Japan* (North-Holland, Amsterdam, 1987).

[2] D. G. Haase, R. Velasquez, and A. I. Kingon, in Proceedings of the High-T_c Conference, Chapel Hill, North Carolina, 1987 (unpublished).

[3] J. O. Willis (private communication).

[4] A. P. Ramirez, R. J. Cava, G. P. Espinosa, J. P. Remeika, B. Batlogg, S. Zahwick, and E. A. Rietman (unpublished).

[5] Single-crystal measurements La_2CuO_4 with varying oxygen stoichiometry are in progress at Los Alamos National Laboratory; J. O. Willis, Z. Fisk, and S. Brown (private communication).

[6] F. Holtzberg, D. L. Kaiser, B. A. Scott, T. R. McGuire, T. N. Jackson, A. Kleinsasser, and S. Tozer, *Chemistry of High-Temperature Superconductors,* edited by David Nelson, M. Stanley Whittingham, and Thomas F. George, American Chemical Society Symposium Series No. 351 (ACS, Washington, DC, 1987), p. 79; D. L. Kaiser, F. Holtzberg, B. A. Scott, and T. R. McGuire, Appl. Phys. Lett. **51**, 1040 (1987).

[7] We estimate the range of δ's by comparison of our susceptibility measurements with the data given by Madoka Tokumoto *et al.*, Jpn. J. Appl. Phys. **26**, L1565 (1987).

[8] E. M. Forgan and S. Nedjat, Rev. Sci. Instrum. **51**, 411 (1980).

[9] Guenter Ahlers, Rev. Sci. Instrum. **37**, 477 (1966).

[10] C. C. Tsuei, S. von Molnar, and J. M. D. Coey, Phys. Rev. Lett. **41**, 664 (1978).

[11] U. Gottwick, R. Held, G. Sparn, F. Steglich, H. Rietschel, D. Ewert, B. Renker, W. Bauhofer, S. von Molnár, M. Wilhelm, and H. E. Hoenig, Europhys. Lett. **4**, 1183 (1987); C. Uher and A. B. Kaiser, Phys. Rev. B **36**, 5680 (1987).

[12] Q. Li, C. H. Watson, R. G. Goodrich, D. G. Haase, and

H. Lukefahr, Cryogenics **26**, 467 (1986).

[13]S. E. Inderhees, M. B. Salamon, T. A. Friedmann, and D. M. Ginsberg, Phys. Rev. B **36**, 2401 (1987).

[14]P. P. Freitas and T. S. Plaskett (unpublished).

[15]J. D. Jorgensen, B. W. Veal, W. K. Kwok, G. W. Crabtree, A. Umezawa, L. J. Mowicki, and A. P. Paulikas, Phys. Rev. B **36**, 5727 (1987).

[16]R. O. Pohl, Phase Transition **5**, 239 (1985).

[17]A. C. Anderson, Phase Transition **5**, 302 (1985).

[18]John E. Graebner, Brage Golding, R. J. Schutz, F. S. L. Hsu, and H. S. Chen, Phys. Rev. Lett. **39**, 1480 (1977).

[19]N. Nishida *et al.* (unpublished); R. Birgeneau (private communication).

[20]A linear term due to magnetic interactions has been observed in the magnetically ordered Gd (1:2:3) compound; R. G. Goodrich (private communication).

[21]A. Junod, A. Bezinge, D. Cattani, J. Cors, M. Decroux, O. Fischer, P. Genoud, L. Hoffmann, J.-L. Jorda, J. Muller, and E. Walker, Jpn. J. Appl. Phys. **26**, Suppl. 26-3, 1119 (1987).

[22]D. R. Harshmann, G. Aeppli, E. J. Ansaldo, B. Battlog, J. H. Brewer, J. F. Carolan, R. J. Cava, M. Celio, A. C. D. Chaklader, W. N. Hardy, S. R. Kreitzman, G. M. Luke, D. R. Noakes, and M. Senba, Phys. Rev. B **36**, 2386 (1987).

[23]M. E. Reeves *et al.*, Phys. Rev. B **35**, 7207 (1987); B. D. Dunlap *et al.*, *ibid.* **35**, 7210 (1987); L. E. Wenger *et al.*, *ibid.* **35**, 7213 (1987); E. Zirngiebl *et al.*, Solid State Commun. **63**, 721 (1987).

[24]C. E. Methfessel, G. R. Stewart, B. T. Matthias, and C. K. N. Patel, Proc. Natl. Acad. Sci., U.S.A. **77**, 6307 (1980).

[25]G. A. Thomas, Y. Ootuka, S. Kobayashi, and W. Sasaki, Phys. Rev. B **24**, 4886 (1981).

[26]B. K. Chakraverty, M. J. Sienko, and J. Bonnerst, Phys. Rev. B **17**, 3781 (1978).

[27]C. Uher and A. B. Kaiser (unpublished).

[28]M. A. Kastner, R. J. Birgeneau, C. Y. Chen, Y. M. Chiang, D. R. Gabbe, H. P. Jennssen, T. Junk, C. J. Peters, P. J. Picone, Tineke Thio, T. R. Thurston, and H. L. Tuller, Phys. Rev. B **37**, 111 (1988).

[29]S. von Molnár and T. Penney, in *Localization and Metal Insulator Transitions,* edited by Hellmut Fritzsche and David Adler (Plenum, New York, 1985), p. 183.

[30]For example, G. Baskaran, Z. Zou, and P. W. Anderson, Solid State Commun. **63**, 973 (1987).

[31]K. Kumagai *et al.* (unpublished).