PHYSICAL REVIEW B VOLUME 36, NUMBER 4 1 AUGUST 1987

Heat capacity of $YBa_2Cu_3O_{7-\delta}$ at the superconducting transition temperature

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(Received 18 May 1987; revised manuscript received 13 July 1987)

The specific heat of a single phase sample of $YBa_2Cu_3O_{7-\delta}$ is measured over the temperature range 3–400 K, revealing a discontinuity at T_c of $\Delta C_p/T_c=55$ mJ (mole f.u.)$^{-1}$ K^{-2}, where mole f.u. denotes mole formula unit. Magnetic susceptibility measurements give a temperature-independent contribution of 3.06×10^{-4} emu (mole f.u.)$^{-1}$. These two measurements suggest that $\Delta C_p/\gamma T_c$ is near the weak-coupling BCS value of 1.43. Comparable measurements reported by other investigators on this compound and on $La_{1.85}Sr_{0.15}CuO_4$ are cited and discussed.

We report here the change in heat capacity at T_c and the normal state paramagnetic susceptibility for a well-characterized sample of $YBa_2Cu_3O_{7-\delta}$ ($\delta=0.15$). We compare our findings with other results reported for this compound and for $La_{1.85}Sr_{0.15}CuO_4$ and provide thereby a current parametric assessment of the superconducting state in these two intensely studied materials.

The preparation regimen for the $YBa_2Cu_3O_{6.85}$ sample was as follows: (a) 950 °C, 24 h calcine-sintering in flowing O_2 at 1 atm of a green pellet composed of finely ground powders of Y_2O_3, $BaCO_3$, and CuO followed by an air cool; (b) crushing, regrinding, and remixing of the sintered pellet; (c) repelleting and resintering at 950 °C in flowing O_2 at 1 atm for 24 h followed by an air cool; (d) 700 °C, 24 h post-sinter heat treatment in flowing O_2 at 1 atm followed by slow cool (over 6 h) to 250 °C.

Meissner-effect measurements at 30 K were made on a sample taken from the heat-treated pellet. The flux-exclusion fraction [flux excluded is calculated[1] with the formula $\phi/\phi_i=-4\pi\chi(1-n)$, where χ is the susceptibility in dimensionless units and n, the demagnetizing factor, taken to be 0], expressed as a percentage of the flux that would be excluded from an ideal superconductor of the same volume as the measured sample, is 61.6%, one of the highest values achieved in the Argonne National Laboratory for a polycrystalline sample. An x-ray diffraction powder pattern made on material taken from the same pellet showed no detectable second phase.

Three calorimeter runs in continuous succession were made in zero field on a 1.6 g sample over the temperature range 3–400 K in a previously described[2] calorimeter that employs the heat-pulse method and incorporates a feedback system to regulate the temperature of concentric radiation shields surrounding the sample. The complete results of this study will be reported elsewhere. In the temperature range pertinent to the work reported here, we have previously stated[3] that results are reproducible to within 0.6%.

The magnetic susceptibility of the specific-heat sample was measured in a superconducting quantum interference device (SQUID) magnetometer. Magnetization measurements taken at 100 K showed a slight curvature at fields below 1 kOe which we take to be due to impurities. The susceptibility was determined at 100, 150, and 200 K from the linear magnetization between 4 and 10 kOe. The susceptibility showed a small temperature dependence of about 10% between 100 and 200 K. A fit of the measured values to the form $\chi=\chi_0+C/T$ gave $\chi_0=3.06\times10^{-4}$ emu (mole f.u.)$^{-1}$, where mole f.u. denotes mole formula unit, and $C=8\times10^{-3}$ emu K (mole f.u.)$^{-1}$, in good agreement with values of χ_0 measured by other authors at other laboratories (see Table I). We correct χ_0 for the diamagnetic core contributions {Y: −12; Ba: −32; Cu^{2+}: −11; and O: −12 [all in units of 10^{-6} emu (mole f.u.)$^{-1}$]} to derive a Pauli susceptibility of 4.92×10^{-4} emu (mole f.u.)$^{-1}$.

We present our calorimetric results in Fig. 1. The data points are those of our third and final run, in which we sought to bracket T_c with closely spaced observations. The solid lines are manually fitted smooth curves derived from the composite data of the three runs, with small up-temperature and down-temperature extrapolations. Taking 93 K as the midpoint of the transition and picking normally conducting and superconducting values from the extrapolated curves at 93 K, we determine $\Delta C_p/T=55$ mJ (mole f.u.)$^{-1}$ K^{-2}. As can be seen from the data points in Fig. 1, our transition is sharp. We believe that this observation together with Meissner-effect and other characterization measurements can be taken to mean that we are

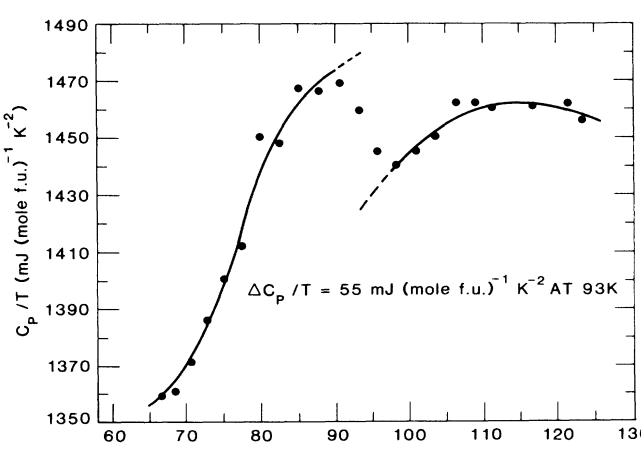

FIG. 1. Heat capacity of $YBa_2Cu_3O_{6.85}$ near the superconducting transition temperature.

TABLE I. Superconducting parameters for $YBa_2Cu_3O_{6.85}$ and $La_{1.85}Sr_{0.15}CuO_4$.

Compound	Measurement method	$\Delta C_p/T_c$ [mJ (mole Cu)$^{-1}$K^{-2}] (T_c)	γ [mJ (mole Cu)$^{-1}$K^{-2}]	$\beta=\frac{\Delta C_p}{\gamma T_c}$ [a]	Reference
$YBa_2Cu_3O_{7-\delta}$	Calorimetry	18 (93 K)	. . .	. . .	Present work
		15 (90 K)	. . .	. . .	4
		13 (92.2 K)	. . .	. . .	5
		$\gtrsim$7 (~92 K)	. . .	. . .	6
	Normal-state susceptibility		12	1.5	Present work
			12	1.2	4
			9	1.4	5
			14	. . .	7
			14	. . .	8
			14	. . .	9
	Critical-field measurements		3		10
			3.7	. . .	11
	Density-of-states calculation		2	. . .	12
			7	. . .	13
$La_{1.85}Sr_{0.15}CuO_4$	Calorimetry	20 (31 K)	. . .	. . .	14
		14,17 (36.5 K)	. . .	. . .	15,16
		24 (~36 K)	. . .	. . .	17
		10 (~37 K)	. . .	. . .	18
	Normal-state susceptibility	. . .	12	. . .	15
	Critical-field measurements	. . .	5–7		19
		. . .	6		20
		. . .	6		21
		. . .	6		22
				~3	
	Density-of-states calculation	. . .	2.2	. . .	23

[a]Note different sources of β values for the two compounds. For $YBa_2Cu_3O_{7-\delta}$, β is based on three sets of ΔC_p and χ_0-derived γ, each reported by the same authors. For $La_{1.85}Sr_{0.15}CuO_4$, β is based on median values of ΔC_p and critical-field-derived γ, reported by various authors.

measuring the properties of a single-phase, homogeneous material.

Our calorimetric result for $YBa_2Cu_3O_{6.85}$ and those of other investigators presently known to us, are shown in Table I. We note first that the spread in T_c is only 3 K; we can conclude that the oxygen stoichiometry is similar for all. To achieve comparability with $La_{1.85}Sr_{0.15}CuO_4$, we express $\Delta C_p/T_c$ in units that represent N_0 (Avogadro's number) of Cu atoms, i.e., in units of mJ (mole Cu)$^{-1}$ K^{-2}. Three of the four values of $\Delta C_p/T_c$ agree to within about 20%. The substantially lower result reported in Ref. 6 should, according to those authors, be regarded as the lower limit of the true value because of the possibility of sample contamination.

It is of interest to evaluate the dimensionless ratio $\beta=\Delta C_p/\gamma T_c$ in order to infer the degree of strong coupling in the high T_c superconductors. A major difficulty in estimating β is the lack of a reliable value of the electronic specific heat γ. Direct measurements of the normal state at low temperature are not possible because the superconductivity cannot be quenched by any magnetic field available in the laboratory. A crude estimate of γ may be obtained from the measured Pauli susceptibility using the free-electron conversion $\gamma/\chi=\frac{1}{3}(\pi k_B/\mu_B)^2$. This estimate does not take into account various enhancements to the susceptibility or specific heat which do not apply to each equally. Therefore, this formula is only a very rough approximation for real materials. The values of γ derived in this way are shown in Table I, and there is agreement to within about 25%, except for the Ref. 10 estimate which appears to be inconsistent with the data upon which it is based.[24] A second method for finding γ, based on the initial slope of the critical field, depends on the dirty limit BCS equations and the measured resistivity. While indirect, this method does not rely on free-electron values of γ/χ and has been shown to work well for low-temperature superconductors.[25] Unfortunately, there are only a few reports in the literature of measurements of $-dH_{c2}/dT$ and ρ on the same sample of $YBa_2Cu_3O_{7-\delta}$ so it is not possible to test the sample dependence and reproducibility of this procedure, or the validity of the dirty limit for these samples. The value of γ derived from the critical field slope given in Table I is lower than those derived from χ suggesting that the estimates from χ may be too high.

However, more experience with this technique is needed before it can be evaluated.

Estimates of γ based on band-structure calculations are also given in Table I for both compounds. These are consistently lower than the experimentally derived values. Interestingly, both superconductors have about the same value of the band structure γ expressed on per mole Cu basis.

The specific-heat jump in $La_{1.85}Sr_{0.15}CuO_4$ has been measured repeatedly on samples whose T_c's are in the range 31–37 K. Values of $\Delta C_p/T_c$ known to us are given in Table I. We note that, expressed in units of mJ (mole Cu)$^{-1}$K^{-2}, the jump lies in the same range for $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_{7-\delta}$.

For $La_{1.85}Sr_{0.15}CuO_4$ there are local moments and antiferromagnetic order in the normal state which depend on the oxygen stoichiometry.[26] Therefore, the Pauli susceptibility and the corresponding value of γ are difficult to extract. Only one estimate of γ seems to have been made from the normal-state paramagnetic susceptibility of $La_{1.85}Sr_{0.15}CuO_4$, and this value is of questionable reliability since χ has an anomalous positive dependence on temperature above T_c. Useful estimates of γ are therefore restricted to values based on the initial critical field slope. The values derived are shown in Table I and are in good agreement with each other.

Values of β can be inferred from the data in Table I. For the ~40 K superconductor $La_{1.85}Sr_{0.15}CuO_4$ we take, respectively, 20 mJ (mole Cu)$^{-1}$K^{-2} and 6 mJ (mole Cu)$^{-1}$K^{-2} as medians for the $\Delta C_p/T_c$ and γ values given in Table I and we find that $\beta \approx 3$, and thus appears to be in the strong coupling limit, as it is larger than the weak coupling value 1.43. On the other hand, there is a narrow range of values bracketing 1.43 for the 90 K superconductor $YBa_2Cu_3O_{7-\delta}$ given in Table I, which are based on measurements having common sample (laboratory) origins. It is tempting to conclude that this material is in the weak coupling limit. However, recent theoretical work by Marsiglio, Akis, and Carbotte[27] shows that as the coupling becomes stronger the value of β first increases, as is usually observed, then unexpectedly decreases, ultimately falling below the weak coupling limit 1.43. Thus, values of β near 1.43 can be obtained in strong coupling as well as in weak coupling, and the results presented above cannot be used to determine which limit is appropriate for $YBa_2Cu_3O_{7-\delta}$.

We gratefully acknowledge valuable discussions and advice from B. W. Veal, B. D. Dunlap, and M. B. Brodsky. The technical assistance of A. G. McKale, J. W. Downey, A. Umezawa, and A. P. Paulikas is acknowledged with thanks. This work was supported by the U. S. Department of Energy, Basic Energy Sciences–Materials Science, under Contract No. W-31-109-ENG-38.

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