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Heat capacity of superconducting $La_{1.85}Sr_{0.15}CuO_4$

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The heat capacity has been obtained for a sample of $La_{1.85}Sr_{0.15}CuO_4$ which is superconducting with a transition temperature $T_c = 31$ K. Although the heat capacity is dominated by the lattice in the vicinity of T_c, it has nonetheless been possible to observe the superconducting transition, thus verifying that this is bulk superconductivity. A lower limit is established for the heat-capacity anomaly of $\Delta C/T_c = (20 \pm 5)$ mJ/mole K^2. Combined with estimates of the electronic heat capacity γ, this leads to $2 \leq \Delta C/\gamma T_c \leq 10$, compared with the Bardeen-Cooper-Schrieffer value of 1.43, which places this material well into the strong-coupling regime.

Recently, high-temperature superconductivity ($T_c = 30$–50 K) has been observed in layered perovskite oxides of the general form $La_{2-x}M_xCuO_4$, with M = Ba or Sr.[1-4] A related system,[5,6] $Ba(Pb_xBi_{1-x})O_3$, has a low electronic density of states with a superconducting transition temperature of $T_c = 13$ K, and one initially expects the electronic density of states to also be low here. If that is so then it becomes difficult to understand the mechanism for superconductivity which would result in transition temperatures up to 50 K. In the initial observations[1] on $La_{2-x}Ba_xCuO_4$ it was suggested that the superconductivity had a percolative nature, or that it arose from two-dimensional fluctuations of the layered perovskite materials. Similarly, it has been suggested[2] that these materials are not bulk superconductors, but that the superconductivity is due to interfacial phenomena. Some of these questions can be resolved by measuring the change in the heat capacity at the superconducting transition temperature. We have carried out such a measurement on two samples of $La_{1.85}Sr_{0.15}CuO_4$. From these data we show that bulk superconductivity is observed, and that the material is in the strong-coupling limit. In addition, evidence is seen for a phase transition at higher temperatures.

The samples were prepared by combining nitrates of the metals with citric acid and ethylene glycol and heating until the nitrates decomposed in a reaction with the organics at about 80–90 °C. The resultant solution was then dried on a hot plate and calcined at 800 °C to form the oxide. The remaining compound was ball milled and a binder consisting of 2–3% polyethylene glycol was added. After spray drying this powder, the samples were dry pressed at 15000 psi and sintered at 1150 °C, resulting in a compact compound having 96% of the theoretical density. Finally, the materials were annealed in oxygen at 500 °C for several hours. Samples prepared in this way give single-phase materials as determined by both x-ray and neutron diffraction. ac susceptibility measurements and resistivity data gave a superconducting transition temperature of 31 K, somewhat less than the value of 36.2 K reported previously for $La_{1.8}Sr_{0.2}CuO_4$,[3] with a transition width of approximately 3 K. This reduction in T_c relative to other work may be related to the presence of oxygen deficiencies in the present compounds, as seen by neutron diffraction.

Heat-capacity data have been obtained on two samples of 2.47 and 10.8 g, independently measured in two different calorimeters which have both been previously described.[7,8] Absolute values between the two sets of measurements agreed very well, and showed good reproducibility. The data for all measurements are combined in Fig. 1, and the region near T_c is shown on an expanded scale in Fig. 2.

Below approximately 4 K, the heat capacity is such that a constant value for $C/T = (5 \pm 1)$ mJ/mole K^2 is obtained. This indicates that not all the sample is superconducting, and this conclusion has also been frequently drawn from Meissner effect measurements on similar samples. In addition, a small peak (not shown in Fig. 1) is seen at temperatures near 0.1 K, perhaps due to the presence of a very minor magnetic impurity. As the temperature is increased, the heat capacity rises, but only shows the C/T vs T^2 behavior one expects for a normal metal for $4 < T < 7.5$ K. In the vicinity of T_c, the heat capacity is very large due to phonon contributions, and the observation of an anomaly due to superconductivity is expected to be difficult, but inspection of the data shows that such an

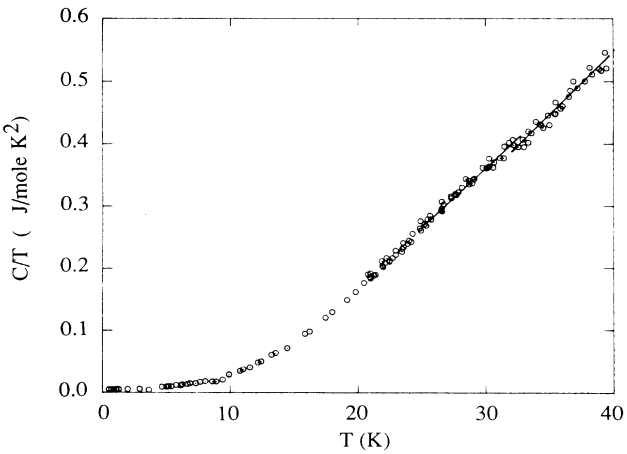

FIG. 1. Heat capacity of $La_{1.85}Sr_{0.15}CuO_4$. Straight lines are drawn to show the change in C/T at T_c.

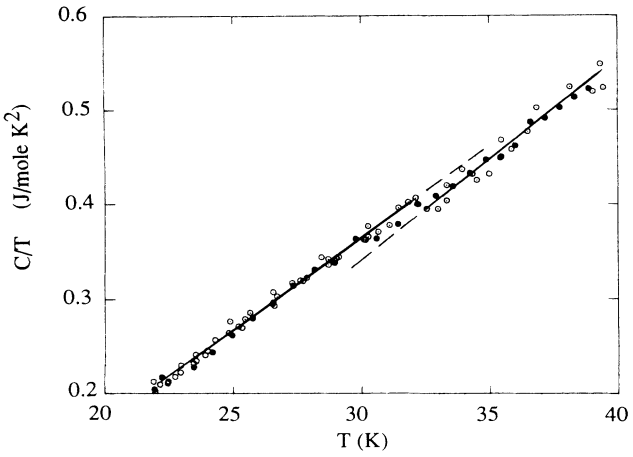

FIG. 2. Heat capacity of $La_{1.85}Sr_{0.15}CuO_4$ near the superconducting transition temperature. Filled circles show the data for a single temperature scan.

effect is clearly present. In individual temperature scans, the change is very apparent, as shown by the filled circles in Fig. 2, although still apparent in the combined data of several runs (open circles). In order to emphasize the change at T_c, straight lines have been drawn through the data for those segments slightly above and below T_c, as shown in the figures. It is then clear that a simple continuation of the data through the transition region is not possible. This effect is repeatable in many scans through the transition region, and is independently observed in the data sets taken on the two calorimeters. From the two line segments we estimate $\Delta C/T_c = (20 \pm 5)$ mJ/mole K^2.

Because of the large value of T_c, an appropriate model for the lattice heat capacity is required to extrapolate the normal-state heat capacity to $T=0$ K, and so obtain an experimental value of the electronic heat-capacity coefficient γ. Attempts to model the data with an exponential temperature dependence for the electronic contribution below T_c, and a Debye function for the phonons, have not given reasonable results, and a derived value of γ from these data is not possible at this time. Using measurements of the initial slope of the critical field versus temperature and estimates of the Fermi surface area based on theoretical calculations,[9] Kwok *et al.* have estimated[10] that $4.9 < \gamma < 7.3$ mJ/mole K^2. With those values and the current result we obtain $\beta = \Delta C/\gamma T_c = 2$–$5$. Since Meissner-effect measurements on similar materials commonly give about 50% flux exclusion, indicating that roughly half the material is superconducting, it may be necessary to increase the experimental value by as much as a factor of 2. We therefore estimate the value of $\Delta C/\gamma T_c = (2$–$10)$ mJ/mole K^2 for $La_{1.85}Sr_{0.15}CuO_4$.

Since the corresponding value for β from the Bardeen-Cooper-Schrieffer (BCS) theory is 1.43, we must consider these to be strong-coupling superconductors, even with our lower estimate. Experimental values of β for compounds which are generally described as strong-coupling superconductors generally fall in the range of 2.5–3 (see Table I for typical results), which are in the lower range of our estimate for the present material. However, it should be noted that strong-coupled superconductors with large values of T_c may be expected to have large heat-capacity discontinuities if the pertinent phonon energies are comparable with other materials. Kresin and Parkhomenko have shown[19] that one can utilize the Eliashberg equation to give the expression

$$\beta = \Delta C/\gamma T_c = 1.4\{1 + 1.8[\ln(\omega/T_c) + 0.5](\pi T_c/\omega)^2\}\ , \qquad (1)$$

where ω is a characteristic frequency for the phonons which are involved in the superconductivity. For a material such as Pb, where $\beta = 2.7$, this expression gives $\omega = 4.5$ meV, in correspondence with the lower peak in $\alpha^2F(\omega)$ as determined by tunneling data. Similar values for ω can be obtained for several other strong-coupled materials. If phonons at this frequency are also the important ones for a material having $T_c = 30$ K, Eq. (1) gives $\beta \sim 10$, corresponding to our upper estimate from the experimental results. In order to have $\beta = 2$ with $T_c = 30$ K, we would need characteristic phonon frequencies with $\omega \sim 25$ meV playing a major role in establishing the superconductivity. Kresin and Parkhomenko also give strong coupling corrections to the energy gap Δ_0. Using that result and the above estimates, we obtain $\Delta_0/k_BT_c = 2.0$–3.5, compared to the BCS result of 1.76. For $T_c = 30$ K, this gives $2\Delta_0 = 10$–18 meV. Heat-capacity data are currently being obtained on compounds which have the same structure but lower values of T_c in order to obtain better values of γ and of the lattice contribution to the heat capacity in the lower temperature region.

For temperatures above T_c, we have evaluated the data assuming an isotropic three-dimensional Debye model. This analysis gave Debye temperatures $\Theta_D \sim 450$ K for $T = 90$ K, decreasing to $\Theta_D \sim 330$ K for $T = 35$ K. If we ignore the changes in the electronic heat capacity below T_c, analysis of this type shows Θ_D reaching a minimum of 320 K at $T \sim 25$ K then rising to $\Theta_D \sim 450$ K at $T = 5$ K. This general behavior for the temperature-dependent Debye temperature is not uncommon in ternary oxides.[20,21] Above 90 K, however, the data were not reproducible under successive temperature scans. In the initial heating through the region 80 K $< T <$ 150 K, a large amount of

TABLE I. Experimental values of $\beta = \Delta C/\gamma T_c$ for strong-coupling superconductors.

Compound	γ (mJ/mole K^2)	$\Delta C/\gamma T$	Refs.
Nb_3Sn	52.4	2.4	11
	35	3.4	12
Nb_3Ge	30.3	2.3	13
Nb_3Al	30.1	2.5	14
Nb_3Si	7.7	2.0	15
Mo_6Se_8	47.2	2.28	16
$Cu_{1.8}Mo_6S_8$	36.9	2.63	17
Pb	3.0	2.71	18
$La_{1.85}Sr_{0.15}CuO_4$	4.9–7.3	2–10	10 and present work

scatter is seen in the heat capacity, with at least two apparent discontinuities, and a similar behavior recurred in the second warming. However, on third and fourth warming cycles the heat capacity varied much more smoothly through the same temperature region. This phenomenon is still under study, but we tentatively suggest that a phase transition occurs at $T \sim 80$ K, which is not fully transformed in a single heating cycle.

In conclusion, heat-capacity measurements have been obtained for samples of $La_{1.85}Sr_{0.15}CuO_4$ which show the appearance of bulk superconductivity. Analysis of the data based on the currently available parameters gives $\Delta C/\gamma T_c \sim 2-10$, which places this material well into the strong-coupling limit of superconductivity. Additional work is currently underway to obtain improved values for the electronic heat-capacity coefficient, to obtain a better description of the phonon contribution to the specific heat, and to investigate the possibility of phase instabilities at temperatures above T_c.

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