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Absence of specific-heat anomaly at the superconducting transition in $La_{1.8}Ba_{0.2}CuO_{4-y}$

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Calorimetric measurements between 2 and 95 K show no specific-heat anomaly at the superconducting transition temperature of 28 K in $La_{1.8}Ba_{0.2}CuO_{4-y}$ within our 1% resolution. This indicates that the total condensation energy associated with the superconducting transition is either very small, possibly resulting from only those electrons in interfacial (two-dimensional) layers, or zero as a result of a different mechanism for bulk superconductivity.

Recently, considerable interest in high-temperature superconductors has been stimulated by the possible superconductivity observed in La-Ba-Cu-O by Bednorz and Müller.[1] Refinements in the sample preparation have led several workers[2-6] to claim the presence of bulk superconductivity in La-Ba-Cu-O and La-Sr-Cu-O systems at temperatures from 18 to 40 K. The major experimental evidence for the bulk superconductivity in these ceramic oxide compounds is the diamagnetism measured by the ac susceptibility being a sizeable fraction of the ideal diamagnetic value for temperatures well below the critical temperature T_c.

It is well known that magnetic measurements can be misleading as to the amount of the material in the superconducting phase. The disappearance of electrical resistance or even the appearance of a strong diamagnetic susceptibility in an ac or dc magnetic field can result from a minority phase that happens to exist in connected loops throughout the sample. This would give rise to zero resistance and a complete diamagnetic signal throughout the volume of the sample corresponding to screening all or most of the applied flux. Heat capacity is a more reliable measurement because it is an extensive property and not as sensitive to trace phases.[7] Typically, the magnitude of the heat-capacity jump at the superconducting transition is directly proportional to the amount of superconducting phase present unless a "gapless" superconductor is found. Thus, the calorimetric measurements reported in this Rapid Communication demonstrate the lack of a specific-heat jump normally associated with a bulk superconducting transition.

The oxide compound investigated in this report had a nominal composition of $La_{1.80}Ba_{0.2}CuO_{4-y}$, which was prepared by the solid-state reaction method under normal atmospheric conditions. The appropriate mixture of La_2O_3, $BaCO_3$, and CuO powders was heated to 900 °C for 8 h in air. After subsequent pulverizing of the reacted mixture, the heating process at 900 °C was repeated for another 6 h. The reacted mixture was then pressed into a pellet at 8000 psi for subsequent sintering. One portion of the pellet was sintered at 1100 °C for 4 h. The remainder was subjected to an isostatic pressure of 60000 psi before sintering at 1100 °C for 4 h. X-ray powder-diffraction patterns of both specimens show the same patterns observed previously[2,3] for this K_2NiF_4-type structure with only a trace ($<5\%$) of the perovskite $CuLaO_3$ phase present. This indicates that these samples are essentially single phase. The heat capacity for samples from each of the two sintering-pressure treatments was first measured before cutting smaller portions for subsequent ac susceptibility and resistivity measurements. The calorimetric and susceptibility results from the 60000-psi treated sample are presented here as there is no essential difference between the data from the two samples.

The resistance was measured by a standard four-probe technique to ensure that a superconducting transition is observed while both in-phase χ' and out-of-phase χ'' components of the ac susceptibility were determined by a mutual inductance technique. The ac measuring frequency was 250 Hz and the driving field was 4.2 mOe. The heat capacity was measured by an adiabatic technique over the temperature range of 2–95 K. The sample holder consisted of a sapphire substrate with an unencapsulated Ge thermometer element which was calibrated against two calibrated thermometers. By comparing the calorimetric measurements on a calorimetric copper sample to the copper reference equation, the error in these measurements is estimated to be less than 1% from 2 to 20 K with the uncertainty increasing to 5% at the highest temperatures. The largest contribution to the uncertainty is the addenda heat capacity which varied from 10% at the lowest temperatures to 20% in the temperature range 4–15 K and then became a smaller fraction at higher temperatures. It should further be noted that the thermal conductance in these sintered samples was fairly high as the heat propagated throughout the samples in less than 5 s below 20 K.

Figure 1 shows the onset of a diamagnetic χ' susceptibility signal at 33 K with a more steeply increasing diamagnetic signal below 28 K. This correlates very well with the onset temperature of 33 K and the zero resistance state at 28 K as determined from the resistance measurements. In larger oscillating magnetic fields, the sharp increase in χ' and the peak in χ'' are spread over a larger

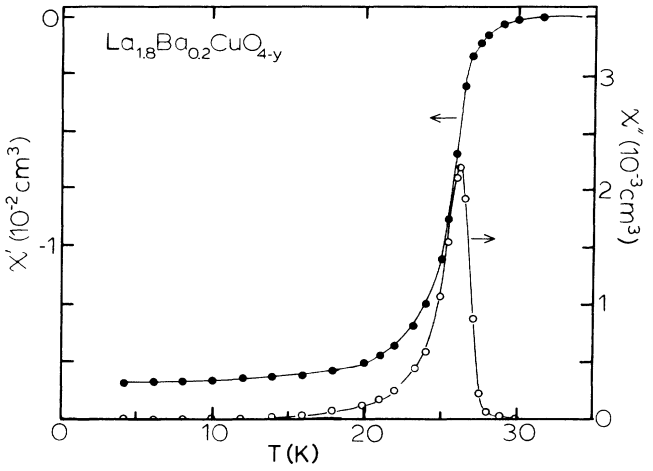

FIG. 1. The in-phase χ'(●) and out-of-phase χ''(○) susceptibilities as a function of the temperature for an oscillating field of 4.2 mOe.

temperature interval. This seems to indicate a fairly granularlike structure with critical currents that can be easily exceeded by the induced currents from the larger ac magnetic fields. At temperatures below 16 K, the in-phase susceptibility appears to approach a constant value, while the out-of-phase susceptibility is negligible. Correcting for the demagnetization shape effects, $D/4\pi = 0.18$, the in-phase χ' component at 4.2 K is $\sim 75\%$ of the ideal $-V/4\pi(1-D)$ value. Even though ac susceptibility measurements cannot distinguish the presence of a bulk Meissner effect[8] as the ac-induced shielding currents would overestimate the percentage of superconducting material, still one would speculate the superconductivity in this sample to be a bulk property.

However, the specific-heat results shown in Fig. 2 show no observable anomaly or jump over the entire temperature region of 2–95 K or within the 1% resolution for temperatures below 35 K. Instead, just a continuously decreasing value of C/T as the temperature decreases is observed. Even if the transition was smeared over several degrees, one would expect to see an observable increase in C/T as various regions became superconducting, e.g., a broad bump. The lack of a specific-heat anomaly would seemingly indicate that the superconductivity is not a bulk property[9] in these oxides. If one maintains the traditional thinking of an energy gap opening up at the Fermi surface for the occurrence of superconductivity, then either a very small fraction of the sample is responsible for the superconductivity, e.g., an interfacial effect in the CuO layers, or the transition is spread over a very broad temperature range. This range would extend over at least the transition region of 28–33 K and could be further broadened by the granular nature of these oxide compounds. A third alternative explanation is that a new mechanism for the appearance of superconductivity in these oxides must be invoked which is based on a non-energy-gap model.

In Fig. 3, the specific heat is shown at temperatures below 8.5 K. The heat capacity of a normal metal for this type of plot would be a straight line with intercept γ and

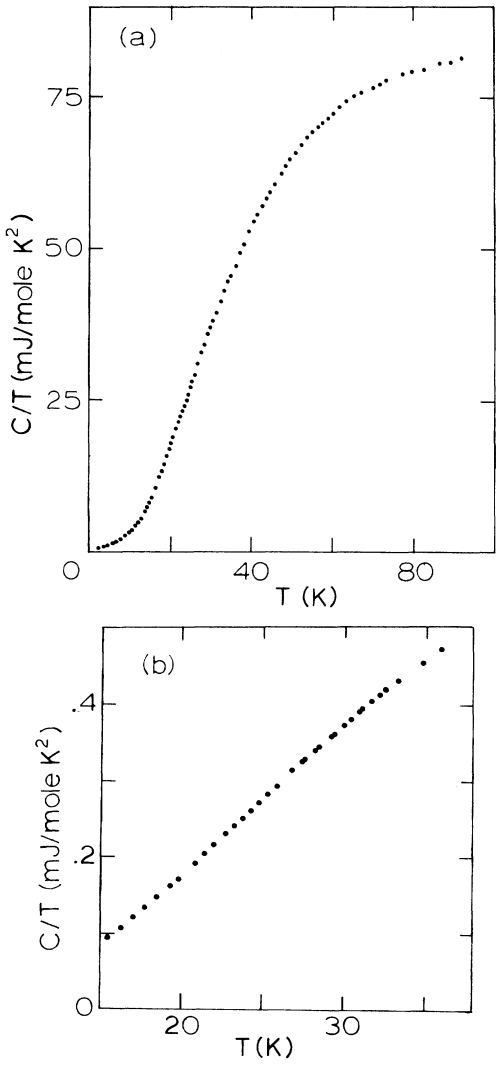

FIG. 2. (a) The specific heat of La-Ba-Cu-O plotted as a function of the temperature over the temperature range of 2–95 K. (b) The specific heat in the vicinity of the superconducting transition of 28 K.

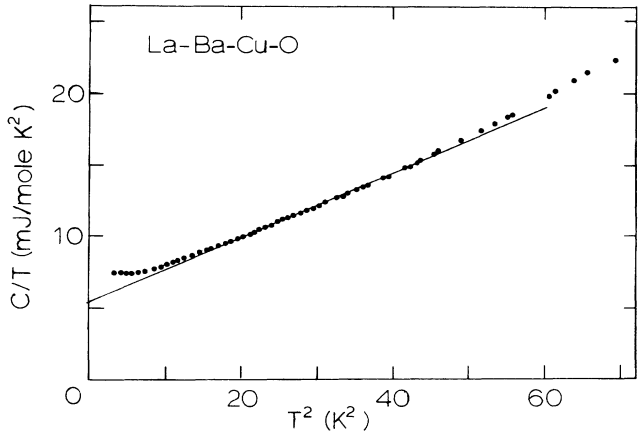

FIG. 3. The low-temperature specific heat plotted as C/T vs T^2. The solid line shows the fit to $C/T = 5.40 + 0.222T^2$.

slope α for the equation $C/T=\gamma+\alpha T^2$. Since there is curvature over the entire temperature range, the data below 6.5 K were found to fit the following: $C=AT^{-2}+\gamma T+\alpha T^3$, where the temperature dependence of the first term is characteristic of the high-temperature limit of a Schottky-like specific heat, the γT term is the electronic specific-heat contribution, and the αT^3 term is the phonon specific heat. The resulting values are $A=9.11$ mJ K/mole, $\gamma=5.40$ mJ/mole K^2, and $\alpha=0.222$ mJ/mole K^4. The presence of a Schottky-like specific-heat term could arise from either magnetic impurities subjected to a crystalline electric field or from a hyperfine field splitting of the La nuclei ($I=\frac{7}{2}$). Since the coefficient A is proportional to both the number of impurities or nuclei and to the square of the splitting between energy levels, one cannot unequivocally determine from this calorimetric measurement that the hyperfine splitting is more realistic. However, since there are 1.8 La nuclei per molecule, a non-negligible nuclear contribution at 4 K seems more plausible. This would then result in a hyperfine splitting of 10.8 mK ($H_{hf}=10.7$ T) between the eight nuclear levels. From the phonon specific-heat coefficient, assuming that there are seven atoms per molecule, a Debye temperature of 394 K is calculated which is not unusually large for oxide compounds. From the electronic term, the density of states for the free-electron model can be calculated for this oxide. The density of states is about 1.15 states/eV per molecule, which is in reasonable agreement with recent electronic band calculations.[10] Again, this value is not large enough to explain the high superconducting temperatures based on conventional BCS theory. In fact, for a BCS superconductor, the specific heat exponentially decreases towards zero as the temperature decreases even in plots of C/T. Thus the presence of the electronic term at $T=0$ K would suggest that the superconducting properties in these oxides may not be simply due to the BCS-type pairing of all the electrons.

In conclusion, the specific-heat measurements show no evidence for a bulk superconducting transition in this La-Ba-Cu-O sample and suggest that a new mechanism might be responsible for the superconductivity that exists in these oxides.

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