Bulk Superconductivity at 36 K in $La_{1.8}Sr_{0.2}CuO_4$

R. J. Cava, R. B. van Dover, B. Batlogg, and E. A. Rietman
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 29 December 1986)

We report the results of resistivity and magnetic susceptibility measurements in $La_{2-x}Sr_xCuO_4$ for $x \leq 0.3$. The $x=0.2$ sample shows a superconducting transition at 36.2 K with a width of 1.4 K. The associated dc diamagnetic susceptibility (Meissner effect) is a large fraction (60%–70%) of the ideal value. We estimate the density of states from critical-field and resistivity data and suggest, by analogy to $BaPb_{1-x}Bi_xO_3$, that conventional phonon-mediated superconductivity can account for the high T_c in this class of materials.

PACS numbers: 74.10.+v, 74.70.Ya

Superconductivity has been observed in a handful of metal-oxide compounds, and is generally made complicated by the fact that a very precise balance of metal valence states and oxygen stoichiometry is necessary to obtain optimal properties. Recently, possible high-T_c superconductivity was reported for a mixture of crystalline phases in the Ba-La-Cu-O system.[1] The properties reported were strongly dependent on annealing conditions, indicating that the variable valence of copper was playing a role. More recently[2,3] the superconducting phase was identified as having the stoichiometry $La_{2-x}Ba_xCuO_{4-y}$ in the tetragonal-symmetry K_2NiF_4 structure type for $x=0.15$. The midpoint of the resistive superconducting transition was found to be 30 K, with the magnetic susceptibility showing a bulk diamagnetic transition at 28 K. Contrary to the initial report, the latter authors found that samples heated in air had superior properties to those heated in Ar, a chemically reducing environment. Here we present the results of our studies on an isostructural phase in a different chemical system, $La_{2-x}Sr_xCuO_4$. As a function of Sr concentration, T_c is highest and the transition is narrowest near $x=0.2$. For this composition the resistive transition is 1.4 K wide (10% to 90%) with a midpoint at 36.2 K and the associated diamagnetic signal approaches bulk values.

$La_{2-x}Sr_xCuO_4$ in the K_2NiF_4 structure type is made of planes of CuO_6 octahedra exclusively sharing corners, separated by (La,Sr)O layers within which the La and Sr are ninefold coordinated to oxygen. The copper-oxygen bonding is very distorted, with the copper actually assuming a planar fourfold coordination with oxygen.[4] For La_2CuO_4, all of the copper is Cu^{2+}, and the structure is a slight orthorhombic distortion of the K_2NiF_4 structure. We have found no superconductivity to 4.2 K in La_2CuO_4. Substitution of Sr (or Ba) for La in small amounts stabilizes the tetragonal, undistorted, K_2NiF_4 structure type, and oxidizes some of the copper to Cu^{3+}, resulting in a mixed-valence compound. The oxygen pressure of the synthetic conditions may therefore exert an influence on the Cu^{3+}/Cu^{2+} valence ratio as well as the charge compensation by oxygen vacancies. We have found, in fact, a dramatic difference in the properties of materials prepared in air, or annealed in pure oxygen at atmospheric pressure.

$La_{2-x}Sr_xCuO_4$ compounds were prepared from the appropriate mixtures of high-purity $La(OH)_3$, $SrCO_3$, and CuO powders, heated for several days in air at 1000 °C in quartz crucibles, with several intermediate grindings. For $x=0.1$ and 0.2, single-phase tetragonal K_2NiF_4-type material was obtained with lattice parameters of approximately $a_0=3.78$ Å and $c_0=13.23$ Å as determined by powder x-ray diffraction. For the $x=0.3$ material there was an increase in c_0 from $x=0.2$, but an extra diffraction peak on the order of 2%–3% of the maximum major-phase intensity was observed, suggesting that the limiting stoichiometry of the K_2NiF_4-type phase prepared in air at 1000 °C is just below $x=0.3$. The powders were pressed into pellets and annealed at 1100 °C for 6 h in air, and cooled to room temperature by removing them from the furnace while at the annealing temperature. Portions of the sintered pellets were used for resistivity and susceptibility measurements, and portions were annealed in flowing O_2 at 900 °C for 1 day, cooled to room temperature in the O_2 flow, and characterized to determine the effects of the annealing atmosphere on the observed properties.

Resistivity measurements were made in a four-probe configuration using silver-paint or silver-epoxy contacts. Because the geometry of the samples is irregular and because the ceramic samples are not perfectly dense, absolute values for the resistivity can only be estimated to roughly 20%, though relative changes in ρ can be measured more precisely. The resistivity just above T_c for the $x=0.2$ sample annealed in air was roughly 3400 $\mu\Omega$-cm, considerably lower than that reported for the La-Ba-CuO compounds.[1] The onset of the resistive transition is at 36.5 K, with a midpoint of 33.1 K and a resistance below instrumental resolution at 28.5 K. The (10% to 90%) width of the resistivity transition for the air-annealed samples is much narrower for the $x=0.2$ sample (5.3 K) than for the $x=0.1$ sample, while the $x=0.3$ sample had a very broad transition with an onset near 35 K and a midpoint of ~15 K. While $\rho(T)$ for the air-annealed samples is typical for a mixture of metallic and insulating (or semiconducting) regions, the oxygen-annealed samples have a metallic $\rho(T)$ characteristic, as indicated by the solid line in Fig. 1, with a resistance just above T_c of roughly 2300 $\mu\Omega$-cm. The transition width is dramatically narrower (1.4 K), the midpint is shifted up to 36.2 K, and the onset temperature is roughly 38.5 K. This change shows the sensitivity of the Cu^{3+}/Cu^{2+} ratio and the superconducting properties to the oxidizing conditions: The presence of the Sr alone as an oxidant for Cu^{2+} is not sufficient to maintain the Cu^{3+} under the synthetic conditions employed.[5]

The critical current of both $x=0.2$ samples is quite low, which may be an indication of inhomogeneity in the samples. Measurements of $\rho(T)$ taken with a current density $j\sim 10^{-1}$ A cm^{-2} gave identical results as measurements taken with $j\sim 10^{-2}$ A cm^{-2}, but a current density of roughly 1 A cm^{-2} was sufficient to depress the resistive transition by about 1.5 K.

The variation of $\rho(T)$ with an applied magnetic field is complex for the air-annealed $x=0.2$ sample and will be described in detail elsewhere. The data indicate that the upper critical field, $H_{c_2}(T)$, of the bulk material is fairly large, with a temperature dependence $-dH_{c_2}(T)/dT|_{T_c}=5$ kOe K^{-1}. The effects of granular structure in this ceramic material, presumably involving Josephson coupling across grain boundaries, can be seen in fields as low as 9 Oe. For the sample annealed in O_2, a similar behavior is observed, with the same upper-critical-field slope near T_c. As in the air-annealed sample, where the effect of microstructural inhomogeneity is evident in $\rho(T)$, similar inhomogeneities may affect the measured $\rho(T)$ in the oxygen-annealed sample. The resistivity can therefore not be employed in conjunction with the upper-critical-field slope to infer a density of states at the Fermi level. A more reliable procedure, discussed below is to measure both the upper and lower critical fields, use these to estimate the thermodynamic critical field, and from this infer the density of states.

The magnetization of the samples was measured in a SQUID magnetometer using two protocols: Either the sample was cooled in zero field and a small field (~10 Oe) was then applied, or else the sample was cooled in the presence of the field. The resulting diamagnetic signals are different, as expected for this type of sample. Most important, however, are the sharp drop at the onset of superconductivity and the magnitude of the signal. For the air-annealed samples, T_c is inferred to be 28, 33, and 15 K for $x=0.1$, 0.2, and 0.3, respectively. The data for the oxygen-annealed sample with $x=0.2$ are given in Fig. 2, illustrating the sharp drop of the magnetization at 36 K. Applying the field after cooldown gives 60%–70% of the full diamagnetism calculated for an ideal superconductor of the same volume. Considering the porosity of our ceramic samples, we conclude that their superconductivity is essentially a bulk property.

No definitive conclusion on the microscopic origin of such high transition temperatures can be drawn at this point, but we suggest that they are due to the ordinary electron-phonon interaction. This is based on analogy with the high T_c in $Ba(Pb,Bi)O_3$, which is 3–4 times

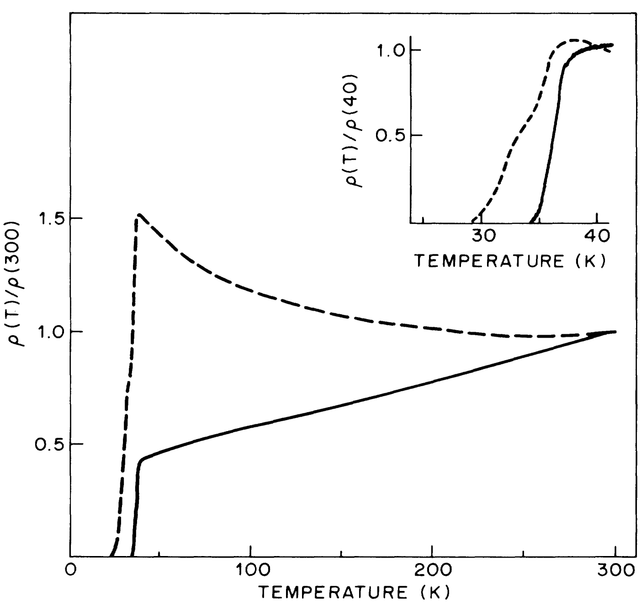

FIG. 1. Resistivity of $La_{1.8}Sr_{0.2}CuO_4$ as a function of temperature, normalized to ρ_{300}, the value at 300 K. The dotted curve is for the sample annealed in air ($\rho_{300}\sim 2200$ $\mu\Omega$-cm), while the solid line was obtained for the sample annealed in oxygen ($\rho_{300}\sim 5500$ $\mu\Omega$-cm). Inset: expanded view of the resistive transition for the same two samples. The vertical axis is now normalized to ρ(40 K).

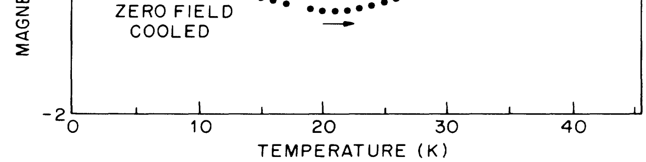

FIG. 2. Temperature dependence of the susceptibility of the oxygen-annealed $La_{1.8}Sr_{0.2}CuO_4$ sample. The susceptibility for the sample cooled in zero field is 60%–70% of the ideal diamagnetic value.

higher than in other superconductors with similar coupling strengths and values for the density of states at the Fermi level.[6–8] There it is the high frequency ($\sim\theta_D$) of the "breathing"-type phonon mode that is essential[9] for the enhanced T_c. In the present compound, Cu is surrounded by (distorted) oxygen octahedra and thus similar modes that modify the O—Cu bond can support a high T_c. On the assumption of the same electron-phonon coupling strength in $La_{2-x}Sr_xCuO_4$ as in $BaPb_{1-x}Bi_xO_3$, a higher density of states would give a higher T_c. Indeed, we have experimental support for this idea. Preliminary low-field measurements of $-dH_{c_2}(T)/dT\,|_{T_c}$ in our samples yield a value which is comparable to that found for $BaPb_{1-x}Bi_xO$, 7 kOe K^{-1}, so that we estimate H_{c_2} to be at least 100–150 kOe at $T=0$. The lower critical field, H_{c_1}, in the present sample is 80–100 Oe at 10 K. Thus, the thermodynamic critical field ($H_c\sim4$ kOe) is 4–5 times higher than in $BaPb_{1-x}Bi_xO_3$, and we conclude that the density of states at the Fermi level is also higher by a factor of 2 ± 0.5, although it is still rather small in absolute units (3 ± 1 mJ $mole^{-1}$ K^2). Within the framework of this discussion, we therefore conclude that conventional phonon-mediated superconductivity accounts for the high T_c also in this class of materials.

The authors would like to acknowledge discussions concerning this work with F. Hellman, D. W. Murphy, C. E. Rice, R. S. Roth, L. F. Schneemeyer, and C. M. Varma, and particularly with J. P. Remeika. We would also like to thank K. Kitazawa for communicating his results prior to publication.

[1]J. G. Bednorz and K. A. Muller, Z. Phys. B **64**, 189 (1986).

[2]S. Uchida, H. Takagi, K. Kitazawa, and S. Tanaka, to be published.

[3]H. Takagi, S. Uchida, K. Kitazawa, and S. Tanaka, to be published.

[4]J. M. Longo and P. M. Raccah, J. Solid State Chem. **6**, 526 (1973).

[5]Further optimization of the preparation conditions has yielded a sample with $x=0.15$ which exhibits a resistive midpoint of 37.5 K, an onset at 40 K, and a full superconductivity at 36 K, as confirmed by dc susceptibility measurements. A sample with $x=0.075$ gave a clear onset at 52 K, a midpoint of 34 K, and zero resistance at 26.5 K.

[6]B. Batlogg, J. P. Remeika, R. C. Dynes, H. Barz, A. S. Copper, and J. P. Garno, in *Superconductivity in d- and f-Band Metals,* edited by W. Buckel and W. Weber (Kernforschungszentrum Karlsruhe, Karlsruhe, West Germany, 1982), p. 401.

[7]B. Batlogg, Physica (Amsterdam) **126B**, 275 (1984).

[8]S. Uchida, K. Kitazawa, and S. Tanaka, to be published.

[9]L. F. Matheiss and D. R. Hamann, Phys. Rev. B **28**, 4227 (1983), and **33**, 823 (1986).