

Normal- and superconducting-state properties of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$

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We report results of resistivity, magnetoresistance, transition-temperature, and upper-critical-field measurements of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. We derive values for the coherence length, mean free path, and electronic specific heat and compare our results with those for $\text{Ba}(\text{Pb,Bi})\text{O}_3$. We conclude that phonon-mediated superconductivity can explain the high transition temperatures in these materials.

The recent discovery¹ of high- T_c superconductivity in $(\text{La},M)_2\text{CuO}_4$ alloys where $M = \text{Ba}, \text{Sr},$ and Ca has created strong interest²⁻⁷ in the basic properties and mechanisms for superconductivity in this class of materials. The layered perovskite structure of these alloys contains a two-dimensional network of oxygen octahedra which is related to the three-dimensional perovskite structure of $\text{Ba}(\text{Pb,Bi})\text{O}_3$, another anomalously-high- T_c superconductor. The Fermi surfaces of both materials show nesting features^{7,8} which are thought to couple to low-energy phonons which drive either superconductivity^{8,9} or metal-semiconductor phase transitions.⁵ The samples of $(\text{La},M)_2\text{CuO}_4$ alloys presently available are polycrystalline sintered aggregates whose properties vary widely with preparation technique. In particular, the samples exhibit many properties characteristic of granular superconductors¹⁰ and measurements are often more sensitive to the coupling between particles than to the intrinsic behavior of the bulk material.

In order to better characterize the superconducting- and normal-state properties of the $(\text{La},M)_2\text{CuO}_4$ alloys, we have performed detailed measurements of the normal-state resistivity, superconducting transition temperature, and upper critical field in a sample of $(\text{La}_{1.85}\text{Sr}_{0.15})\text{CuO}_4$ which has an unusually low resistivity. The low resistivity means that the particles are relatively well coupled so that our measurements better approximate the intrinsic behavior of these materials. We derive the zero-temperature critical field, the coherence length, the mean free path, and limiting values of the normal-state electronic specific heat. We compare our results with those for $\text{Ba}(\text{Pb,Bi})\text{O}_3$ and discuss the possibility of phonon-mediated superconductivity.

The samples were prepared by a coprecipitation technique followed by pressing and sintering. Soluble nitrates of La, Cu, and Sr were mixed in solution in their correct proportions. The materials were coprecipitated as insoluble carbonates and hydroxycarbonates through the addition of sodium carbonate solution. The precipitate was centrifuged, washed, and dried overnight at 140°C. The dried powder mixtures were then fired at 825°C for 2 h to form the oxides which were then pressed to approximately 60% of the theoretical density and sintered at 1100°C in air for 4 h. The resulting pellets were generally about 80% of the theoretical density of 7.14 g/cm³. Following this preparation, our sample was oxygen annealed at 500°C for 12 h.

The resistivity data were taken by a standard four-probe ac method at 100 Hz with a measuring current of 5 mA, corresponding to a current density of about 0.70 A/cm². Electrical contact was made to the sample through copper wires attached to the sample with conducting silver paste. Data were taken at fixed fields of 0, 4, and 8 T from 4 to 80 K, and at several fixed temperatures from 1 to 45 K in fields from 0 to 8 T.

The temperature-dependent data are shown in Fig. 1. There is a nearly linear temperature dependence between T_c and room temperature with a relatively large resistance ratio of 4.3. The resistivity at T_c is 403 $\mu\Omega$ cm, considerably lower than that in other samples.^{1,4} There is a smooth S-shaped transition into the superconducting state, with no resistive "foot" extending to low temperatures, as has been observed in samples without oxygen annealing.^{1,4,7} The midpoint of the transition is $T_c = 33.4$ K, the 10–90% transition width is 3.17 K, and zero resistivity is achieved at 28.1 K.

The high-temperature side of our transition curve is much more extended than the low-temperature side, suggesting that there may be measurable effects of superconductivity well above T_c . As shown in the inset of Fig. 1,

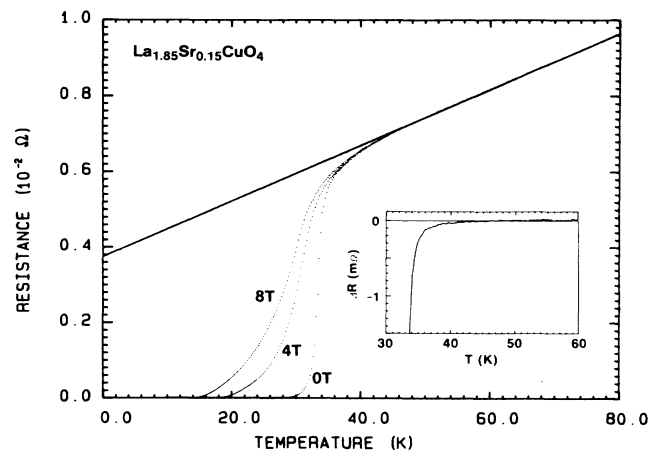


FIG. 1. Electrical resistance vs temperature for $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ in magnetic fields of 0, 4, and 8 T. The solid line is a linear fit to data above 44 K extrapolated to $T = 0$ K. Inset shows the difference curve of $R(H = 0) - R(H = 8\text{ T})$ vs temperature.

there is clear evidence of superconductivity at 42 K. However, no diamagnetism is observed at these temperatures, indicating that only a tiny fraction of the sample is superconducting.

The transition temperature and transition width are strongly dependent on the measuring current. Extrapolation to zero current gives $T_c = 34.6$ K, while at 28.5 mA $T_c = 22.3$ K, and the 10–90% width is 6 K. Extrapolation to higher currents suggests $T_c = 0$ at approximately 65 mA. We do not believe that this depression of T_c with current is necessarily due to poor coupling between superconducting grains, because a similar depression is observed¹¹ in single crystals of $\text{Ba}(\text{Pb,Bi})\text{O}_3$.

In finite magnetic field, the superconducting transition is depressed and considerably broadened, as shown in Fig. 1. At 4 and 8 T, the midpoint of the transition decreases to 30.2 and 28.1 K and the 10%–90% width increases to 10.3 and 14.0 K, respectively. At 10 K and below, the resistivity remained zero within experimental resolution at all fields up to 8 T. At 20 K, a finite resistance first appeared at 2.8 T, as shown in Fig. 2. At 26 K and above, there is a sharp jump in the resistance between zero and 200 Oe, the lowest nonzero value of the field at which data were taken. This sharp jump is followed by a slower increase at higher fields. The normal-state magnetoresistance at 45 K was zero to within 0.3% between 0 and 8 T. The slope in the data at 36 K in Fig. 2 is due to the presence of superconductivity at this temperature.

Critical fields were derived from the data in Figs. 1 and 2 by extrapolating the linear temperature dependence above T_c down to $T = 0$. The 10%, 50%, and 90% transition resistances were determined as a function of temperature from this extrapolation and the corresponding transition fields were obtained. Figure 3 shows that the 50% curve is linear within experimental accuracy, while the 10% curve shows upward curvature near T_c . The increase in transition width with field shown in Figs. 1 and 3 suggests strong anisotropy in the critical field, as expected from the nearly two-dimensional electronic structure⁵ described later. The 50% curve has a temperature derivative at T_c of 1.52 T/K, comparable to that in samples prepared identically to ours but without oxygen annealing.⁶ However,

this value is considerably higher than that reported elsewhere⁴ for $(\text{La}_{1.8}\text{Sr}_{0.2})\text{CuO}_4$.

The orbital critical field at $T = 0$ can be estimated from the Werthamer-Helfand-Hohenberg (WHH) theory^{12,13} using the critical-field slope and T_c . Either the clean- or the dirty-limit form of the theory may be used for this estimate, because the two predictions for $H_{c2}(0)$ differ by less than 2%, yielding a value of approximately 36 T. This value is considerably lower than the Pauli limiting critical field, $H_P = 1.84T_c \sim 61$ T. We conclude that spin effects will not play a role in determining the upper critical fields in these compounds.

The resistivity of our sintered aggregate sample is not intrinsic to this alloy, so that only a lower limit to the mean free path Λ can be derived from our measured resistivity. This lower limit was obtained from the resistivity formula $\rho = 12\pi^3\hbar/e^2\Lambda S$, using the Fermi surface area S from a simple tight-binding treatment of the band structure⁵ which gives a cylindrical Fermi surface of a square cross section characteristic of a nearly-two-dimensional conductor. In this model the Fermi surface area is given by $S = (8\pi^2\sqrt{2})/ac$ where a and c are the unit-cell dimensions, giving $\Lambda > 17$ Å at T_c . The Ginzburg-Landau (GL) coherence length at $T = 0$ can be estimated from the zero-temperature critical field giving $\xi_{\text{GL}} = 30$ –50 Å, depending on whether the sample is assumed to be in the clean or dirty limit. The Bardeen-Cooper-Schrieffer (BCS) coherence length ξ_0^{BCS} , calculated with the values of the electronic specific heat derived below and the Fermi surface area, is also in the same range (see Table I).

Compared to other measurements⁴ on similar alloys, our sample shows a slightly lower transition temperature, a slightly larger transition width, and a critical-field slope at T_c which is higher by a factor of 3 (see Table I). These three features, and especially the larger critical-field slope, strongly suggest that our sample is in the dirty limit. Using our measured resistivity of $403 \mu\Omega \text{ cm}$ in the WHH expression $[-dH_{c2}/dT]_{T_c} = 4.40 \times 10^3 \rho \gamma$ gives a lower limit to the electronic specific-heat coefficient $\gamma = 4.9$

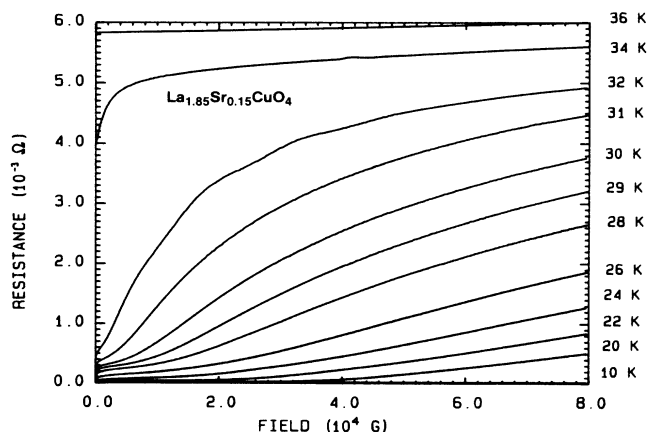


FIG. 2. Resistance vs magnetic field for various temperatures.

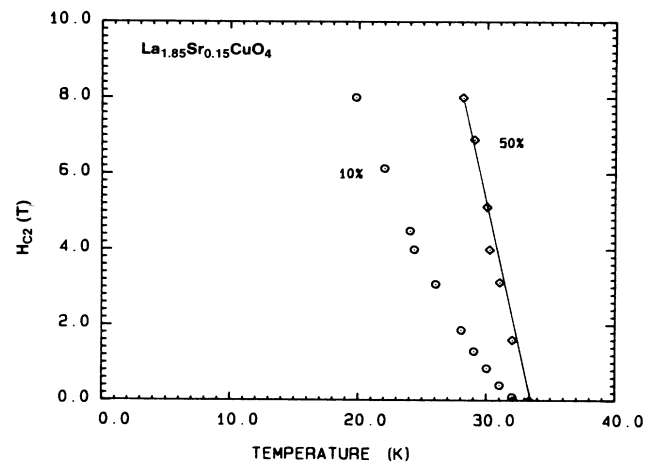


FIG. 3. Phase diagram of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ showing the critical-field data for 10% and 50% transition points. The solid line has a slope of -1.51 T/K.

TABLE I. Comparison of properties of two samples of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with those of $\text{Ba}(\text{Pb}_{1-x}\text{Bi}_x)\text{O}_3$.

	$\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$	$\text{La}_{1.80}\text{Sr}_{0.20}\text{CuO}_4^a$	$\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$
γ (mJ/K ² mole f.u.)	7.31 (clean) 4.90 (dirty)		1.5–1.6 ^{a,b,d}
ξ_{GL} (Å)	30–50		60–79 ($x=0.25$) ^{b,c}
ξ_{BCS} (Å)	34–51		
$H_c^{(0)}$ (T)	36	10–15	~6 ^b
$[-dH_c/dT]_{T_c}$ (T/K)	1.51	0.5	0.5–0.7 ^{b,c}
Λ (Å)	> 17 ($T=T_c$) > 4 ($T=300$ K)		15 ($x=0.2$) ^d
n (10^{21} cm ⁻³)	~5 ^e		2.0–3.2 ^{b,c,d}
$V_{\text{unit cell}}$ (Å ³)	190.1		316.3 ($x=0.216$) ^f
T_c (K)	33.4	36.2	10.7–12 ^{g,h}
$\rho(T_c)$ ($\mu\Omega$ cm)	403	2300	540–1100 ^{b,c,d}
$\rho(300\text{ K})/\rho(T_c)$	4.3	~2	1 ^d
v_F (10^8 cm/s)	0.0834 (clean) 0.124 (dirty)		0.32 ^b
^a Reference 4.	^d Reference 17.		^f Reference 8.
^b Reference 11.	^e Estimated from the Fermi surface		^g Reference 9.
^c Reference 14.	dimensions of Ref. 5.		

mJ/K²mole f.u. Because dirty-limit critical-field slopes are higher than clean-limit slopes, the clean-limit WHH formula

$$[-dH_c/dT]_{T_c} = 1.38 \times 10^{35} (\gamma/S)^2 T_c$$

gives an upper limit to γ . Using the estimate of S described above, we obtain an upper limit of $\gamma=7.3$ mJ/K²mole f.u., remarkably close to the lower limit. Apparently, our sample is not too far from the clean limit, a conclusion well supported by our estimates of the mean free path and coherence length.

Some insight into the origin of the high T_c in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ can be obtained from the comparison with $\text{Ba}(\text{Pb,Bi})\text{O}_3$ given in Table I. Each material is composed of oxygen octahedra which have characteristic rotational, breathing, and tipping phonon modes, and each shows structure in the phonon density of states^{15,16} at relatively low energies, below 11 meV. As a first approximation, we take the phonon properties of these two materials to be similar. However, there are important differences in the electronic properties. $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is a layered compound with a nearly two-dimensional Fermi surface containing large flat regions allowing nearly all the electrons to participate in the nesting, while $\text{Ba}(\text{Pb,Bi})\text{O}_3$ is a three-dimensional compound with a rounded Fermi surface where nesting features involve only a fraction of the electrons. Therefore, we expect the electron-phonon interaction induced by nesting to be stronger in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ than in $\text{Ba}(\text{Pb,Bi})\text{O}_3$. Our measurements show that γ is a factor of 3–5 larger in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ than in $\text{Ba}(\text{Pb}_{0.8}\text{Bi}_{0.2})\text{O}_3$.^{9,11} This large value of γ could be due to a van Hove singularity in the band structure of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ as proposed elsewhere,⁵ or to a larger electron-phonon renormalization. In any case, the larger

enhanced density of states is the major difference between the two materials and is responsible for the much higher T_c 's observed in the $(\text{La},M)_2\text{CuO}_4$ alloys.

To test whether a phonon-mediated mechanism for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is possible, we use the McMillan factorization formula^{18,19}

$$\lambda = N(E_F) \langle I^2 \rangle / M \langle \omega^2 \rangle = \alpha \gamma_b,$$

where $N(E_F)$ is the band density of states per unit volume and γ_b is the corresponding electronic specific-heat coefficient. As a rough estimate, we assume that the phonon properties of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ are similar to those of $\text{Ba}(\text{Pb,Bi})\text{O}_3$, so that the values of λ for the two materials simply scale by the band density of states. Taking $\lambda=1.2$ (Ref. 20) and $\gamma_b=7.88$ J/m³K² (Ref. 8) for $\text{Ba}(\text{Pb}_{0.75}\text{Bi}_{0.25})\text{O}_3$ gives $\alpha \cong 0.15$ m³K²/J. Using $\gamma=(1+\lambda)\gamma_b=(1+\lambda)\lambda/\alpha$ we arrive at estimated values of λ in the range 3.1–3.9 for $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. For strongly coupled systems the relation between T_c and λ is roughly linear if the phonon spectrum is unchanged.^{18,21} Assuming that the phonon properties of the two materials are similar, we may scale T_c for $\text{Ba}(\text{Pb,Bi})\text{O}_3$ by the ratio of the λ values to obtain T_c for $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ in the range 34–42 K. We conclude that if the electron-phonon interaction produces the superconductivity in $\text{Ba}(\text{Pb,Bi})\text{O}_3$, it is also capable of producing high- T_c superconductivity in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$.

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