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Transport properties of the superconducting oxide $La_{1.85}Sr_{0.15}CuO_4$

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We report electrical-resistivity, Hall-effect, and thermoelectric-power (TEP) measurements on the superconducting oxide $La_{1.85}Sr_{0.15}CuO_4$. The transport properties indicate that in the normal state the material conducts via holes with a carrier concentration of 6.0×10^{21} cm^{-3}. Evidence is observed for unusual phonon-drag effects above the superconducting transition temperature T_c and granular or inhomogeneous superconductivity in the vicinity of T_c. Below T_c the resistivity, Hall constant, and TEP all drop to zero, as expected for a superconducting ground state.

There is enormous interest in the alloyed conducting lanthanum-copper-oxides $La_{2-x}M_xCuO_4$ (M = Ba, Ca, Sr) first shown to be superconducting by Bednorz and Müller.[1] A great deal of research has been initiated to characterize this class of material and to understand their associated high-temperature superconducting transition. It has been suggested that the materials in this class with the highest transition temperature and narrowest transition width can be obtained by replacing 7.5% by weight of the La in La_2CuO_4 with Sr.[2,3] Related studies have examined the normal and superconducting state of La_2CuO_4 and $La_{2-x}M_xCuO_4$. These include investigations of the transition temperature,[4,5] the critical field,[6] the band structure,[7,8] and the energy gap.[9] Although novel mechanisms for the high-T_c superconductivity have been suggested,[10,11] at present the theoretical situation is unsettled. However, no strong evidence against the BCS mechanism has been presented.

We have attempted to more fully characterize the normal and superconducting state properties of $La_{1.85}Sr_{0.15}CuO_4$ through electrical-resistivity, Hall-effect, and thermoelectric-power (TEP) measurements, performed between 4.2 and 300 K. Below the superconducting transition temperature $T_c = 38$ K, the behavior of the resistivity, Hall effect, and TEP are generally as expected for a superconductor. In the normal state above T_c, the transport coefficients indicate positive charge carriers with a concentration $n = 6\times10^{21}$ cm^{-3}. The TEP behavior above T_c is unconventional and suggests unusual phonon-drag effects. The Hall constant shows a sharp anomaly near T_c which may be indicative of granular superconductivity.

Samples of $La_{1.85}Sr_{0.15}CuO_4$ were prepared by combining stoichiometric proportions of La_2O_3, CuO, and $SrCO_3$ and heating the mixture to 1100 °C for 5 h. The mixture was then reground and pressed into a pellet and sintered at 1100 °C for 24 h. After sintering, the polycrystalline sample was slowly cooled to room temperature. X-ray powder diffraction analysis confirmed that the samples were single phase, with the tetragonal structure. Magnetic susceptibility measurements performed on a SQUID magnetometer indicated a volume susceptibility of $\chi_V = -4\times10^{-2} = 0.5(-1/4\pi)$, suggesting that approximately 50% of the sample behaves as a bulk superconductor.

Electrical-resistivity measurements were performed using an ac four-terminal method with indium current leads and silver-paint voltage probes. The Hall effect was measured via a five-contact method,[12] where a low-frequency ac (200-Hz) current source and three current contacts are used to null the zero magnetic field misalignment voltage. The small Hall signal was detected with a low noise impedance matching transformer and a lock-in amplifier. The Hall effect was measured on samples with typical dimensions of 5 mm×2.5 mm×0.15 mm. Electrical contacts were made by using low melting point InSn solder and ultrasonic soldering techniques. The thermoelectric power was measured by using a slow ac heating technique.[13] Small samples, typically 2 mm×0.5 mm×0.2 mm, were mounted in a vacuum between a pair of crystalline quartz blocks and 1-mil gold wires were attached to the sample ends with ultrasonically soldered InSn and Ag paint. Both quartz blocks were wrapped with separate manganin wire heaters which were used to ramp a temperature gradient of varying magnitude and direction across the sample. The temperature gradient was monitored with a chromel-constantan thermocouple. The thermoelectric voltages across both the sample-gold and chromel-constantan thermocouples were amplified with a pair of low-noise amplifiers and then detected with an X-Y chart recorder.

Figure 1 shows the sample resistance measured between 50 and 20 K. The initial deviation from the high-temperature behavior occurs at $T_c^0 = 41$ K, the midpoint

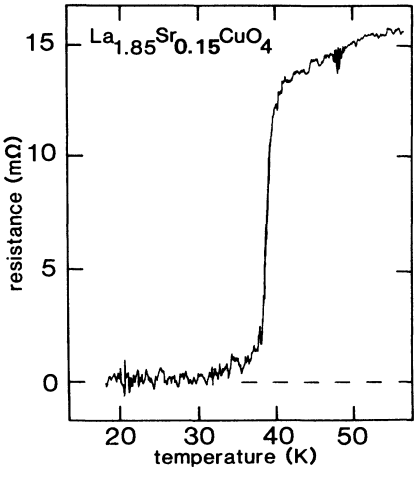

FIG. 1. Resistance of $La_{1.85}Sr_{0.15}CuO_4$ near the 38-K superconducting transition.

of the transition is at $T_c = 38$ K, and the resistance is zero below 33 K. The transition width (90%–10%) is approximately 2 K. These results are in agreement with previous studies on $La_{1.85}Sr_{0.15}CuO_4$.[4]

The results of Hall-effect measurements between 300 and 4.2 K at a magnetic field strength of 10 kG and a current density of 0.23 A/cm^2 are shown in Fig. 2. The Hall constant R_H is positive at all temperatures above T_c. R_H was found to be linear both in field strength (up to 10 kG) and current density (up to 0.23 A/cm^2) at all temperatures examined in this study. The Hall constant R_H is 1.0×10^{-9} m^3/C at room temperature and rises linearly as the temperature drops toward the superconducting transition temperature, taking on a value of 1.8×10^{-9} m^3/C at 45 K. A large anomaly in the Hall voltage is seen at the temperature where the onset of the superconductivity transition is seen in the resistivity. As shown in the inset to Fig. 2, the Hall signal doubles in a span of 2 K, reaching a value of 3.5×10^{-9} m^3/C at $T_{max} = 38$ K. At temperatures below T_{max} the Hall voltage drops towards zero, as expected for a superconductor. We note, however, that between 35 and 32 K the Hall voltage appears to overshoot zero slightly, taking on a nonnegligible negative value with a maximum of -0.12×10^{-9} m^3/C at 33.8 K. Below 32 K the Hall voltage is zero to within the experimental sensitivity of 0.01×10^{-9} m^3/C.

The thermoelectric power of $La_{1.85}Sr_{0.15}CuO_4$ at temperatures between 4.2 and 300 K is presented in Fig. 3. The thermopower is positive at all temperatures, with a room-temperature value of +14.2 μV/K. The TEP displays a broad concave-downward hump centered at 150 K, where the TEP is +20.5 μV/K. Below 150 K the thermopower slowly drops with temperature and reaches a value of +11 μK/V just above the superconducting transition. As shown in the inset to Fig. 3, the TEP drops abruptly to zero around T_c. Below 34 K the thermopower is zero to within experimental uncertainty. The large error bars in the low-temperature data are due to the uncertainty in the thermopower of the gold wire used in the measurement apparatus.[14] This uncertainty arises from the large phonon-drag peak which occurs in gold in this temperature region. Because the exact magnitude and location of the peak is quite dependent on impurity levels, manufacturing methods, etc., for the gold wire, and since the majority of the thermopower voltage comes from the gold wire when the sample is in the superconducting state, a large error can result.[15]

We analyze the Hall effect and TEP results above T_c in terms of the semiclassical model with a single band. For a single band with a general, anisotropic relaxation time τ and a local average Fermi-surface radius of curvature $(\overline{1/\rho})$ the Hall coefficient will be[16]

$$R_H = \frac{12\pi^3}{ce} \frac{\int \tau^2(\mathbf{k}) v^2 (\overline{1/\rho}) ds}{\left[\int \tau(\mathbf{k}) v ds\right]^2} , \qquad (1)$$

where v is the Fermi velocity. With isotropic electron scattering and a spherical Fermi surface, this reduces to the familiar $1/nec$ with a positive value for a holelike Fer-

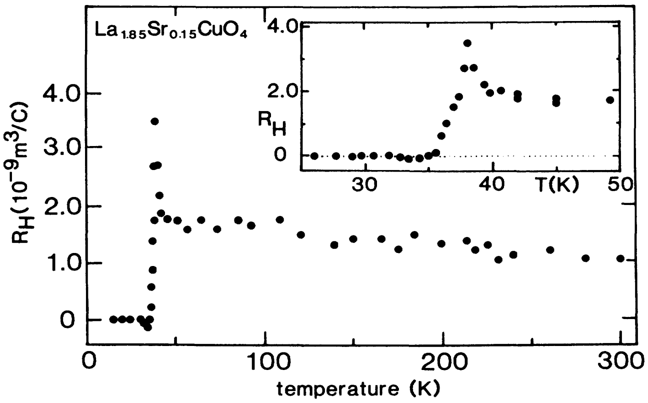

FIG. 2. Hall constant in $La_{1.85}Sr_{0.15}CuO_4$. The inset shows the Hall constant in the vicinity of the 38-K superconducting transition.

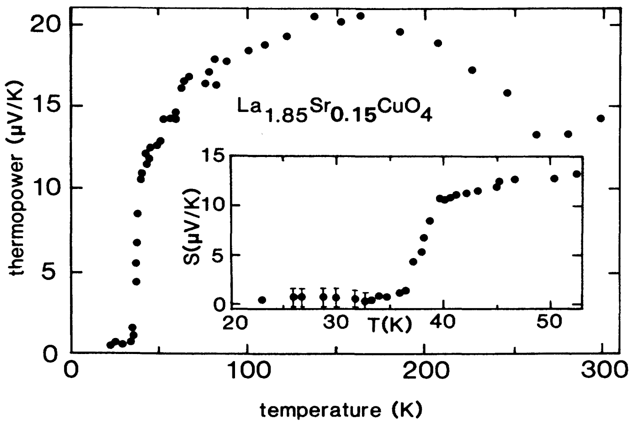

FIG. 3. TEP of $La_{1.85}Sr_{0.15}CuO_4$. The inset shows the TEP in the vicinity of the 38-K superconducting transition.

mi surface and a negative value for an electronlike surface. Hence, the Hall effect measures both the sign of the carriers and the nature of electron scattering; any unusual temperature dependence generally signals that unordinary electronic scattering is taking place.

The diffusion thermopower is related to the dc electrical conductivity σ in the semiclassical model by[17]

$$S_0 = -\frac{\pi}{3}\frac{k_B^2 T}{|e|}\sigma'(E_F)/\sigma(E_F) , \qquad (2)$$

where the derivative is made with respect to energy and is evaluated at the Fermi energy E_F. The conductivity can be related to Fermi-surface parameters as[18]

$$\sigma = \frac{e^2}{12\pi^3\hbar}\tau(E_F)\bar{v}S_F , \qquad (3)$$

where S_F is the Fermi-surface area. The sign of the thermopower will indicate the sign of the majority carrier because of the S_F term in Eqs. (2) and (3). Furthermore, the diffusion thermopower is expected to be linear in temperature; any deviation from linearity indicates that special electronic scattering processes are occurring. In addition to the diffusion thermopower there may exist a phonon-drag thermopower contribution which can give a large enhancement to the total TEP at roughly $\frac{1}{5}-\frac{1}{10}$ the Debye temperature Θ_D. This phonon-drag enhancement usually shows up the TEP as a large peak in the thermopower voltage at low temperatures. Hence, the thermopower of a "normal" metal will be linear in temperature at high temperatures and may exhibit a phonon-drag peak near $T=\Theta_D/10$. In $La_{1.85}Sr_{0.15}CuO_4$, $\Theta_D=413$ K.[19]

Within the confines of the semiclassical model both the Hall effect and thermopower indicate that $La_{1.85}Sr_{0.15}CuO_4$ conducts via holes. The Hall-effect data suggest a hole concentration of 6.0×10^{21} cm^{-3} at room temperature. The lack of features in the temperature dependence of the Hall voltage well above the transition region is typical of metals and appears to indicate that no novel anisotropic temperature-dependent electron scattering occurs in this material. However, the TEP in this temperature region is far different from that expected for a simple metal. In particular, the Seeback voltage is very nonlinear with temperature and the large, broad hump centered about 150 K appears to be both too wide and at too high a temperature to be ascribed to the usual phonon-drag effect. We note that similar unusual TEP results have been seen in such varied materials as the linear chain metal $TaSe_3$ (Ref. 20) and uranium intermetallics,[21] but as yet there is no clear explanation as to its cause. The Hall data for $La_{1.85}Sr_{0.15}CuO_4$ clearly show that no unusual electron scattering is occurring above 50 K; hence, the TEP results must be attributed to something other than simple electron scattering effects. It is possible that the broad hump is a manifestation of special phonon-drag scattering that can only occur when a temperature gradient exists across this material. Elasticity measurements[22] on $La_{1.85}Sr_{0.15}CuO_4$ indicate unusual lattice softening effects; it is possible that soft modes could couple to the charge carriers under a temperature gradient through phonon-drag scattering.[23]

The large, distinct anomaly at the onset of the superconducting transition which occurs in the Hall voltage is reminiscent of that seen in materials undergoing a structural phase transition.[24] This is apparently not the case here because no corresponding anomaly appears in the thermopower. The TEP in $La_{1.85}Sr_{0.15}CuO_4$ instead abruptly drops to zero near T_c, whereas the Hall voltage first sharply rises to double its value and then falls to zero as T is lowered through T_c. It is evident that the Hall anomaly must be a result both of the onset of the superconducting transition and of the presence of the magnetic field. In particular, if superconductivity first occurs in isolated, localized granules, the expelled flux could drastically increase the magnetic field in the normal regions resulting in a large enhancement of the Hall voltage. As the temperature drops further, these superconducting granules should grow in size until a percolation threshold is surpassed at which point the granules join to form complete sections of the "bulk" superconductor. When this occurs the material would act like a conventional superconductor, giving rise to a turn around towards zero in the Hall voltage. This scenario of granular or inhomogeneous superconductivity is particularly plausible in light of the fact that these ceramic oxide materials are somewhat porous in nature; hence, inhomogeneities are likely.

Both the thermopower and the Hall voltage drop to zero below the superconducting transition in accord with the behavior expected for a superconducting ground state. The Hall voltage appears to overshoot zero between 32 and 35 K; this could be another result of the inhomogeneous nature of the sample although it could also be due to the type-II nature of this superconductor. Below 32 K the Hall voltage is clearly zero.[25]

In conclusion, the Hall effect and thermopower of $La_{1.85}Sr_{0.15}CuO_4$ show the material to be holelike in its normal state. The Hall voltage indicates that there may exist granular or inhomogeneous superconductivity in this material. Although a good deal of experimental and theoretical research has been done on granular superconductors[26] we are not aware of any studies of the Hall effect in these types of materials. The development of a theory to describe the Hall effect near the onset of superconductivity in a granular superconductor would be a fruitful line of research. The thermopower suggests that novel phonon-drag scattering processes occur in the normal state of $La_{1.85}Sr_{0.15}CuO_4$ in the presence of a temperature gradient. The results below T_c are in accord with a superconducting ground state in $La_{1.85}Sr_{0.15}CuO_4$ below T_c.

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

[2] R. B. van Dover, R. J. Cava, B. Batlogg, and E. A. Rietman, Phys. Rev. B **35**, 5337 (1987).

[3] K. Kishio, K. Kitazawa, S. Kanbe, I. Yasuda, N. Sugii, H. Takagi, S. Uchida, K. Fueki, and S. Tanaka (unpublished).

[4] R. J. Cava, R. B. van Dozer, B. Batlogg, and E. A. Rietman, Phys. Rev. Lett. **58**, 408 (1987).

[5] C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang, Phys. Rev. Lett. **58**, 405 (1987).

[6] D. W. Capone II, D. G. Hinks, J. D. Jorgensen, and K. Zhang (unpublished).

[7] J. Jun, A. J. Freeman, and J. H. Xu (unpublished).

[8] L. F. Mattheiss, Phys. Rev. Lett. **58**, 1028 (1987).

[9] U. Walter, M. S. Sherwin, A. Stacy, P. L. Richards, and A. Zettl, Phys. Rev. B **35**, 5327 (1987).

[10] P. W. Anderson (unpublished).

[11] V. Kresin (unpublished).

[12] R. H. Friend and N. Bett, J. Phys. E **13**, 294 (1980).

[13] P. M. Chaikin and J. F. Kwak, Rev. Sci. Instrum. **46**, 218 (1975).

[14] The experiment measures only the difference in TEP between the sample and the gold wires. Hence, any uncertainty in the absolute TEP of the gold leads to an uncertainty in the TEP of the sample.

[15] R. L. Crisp, Philos. Mag. **10**, 553 (1964).

[16] C. M. Hurd, *The Hall Effect in Metals and Alloys* (Plenum, New York, 1972), p. 75.

[17] N. F. Mott, Proc. R. Soc. London, Ser. A **156**, 368 (1936).

[18] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge Univ. Press, London, 1972), p. 218.

[19] N. Phillips (private communication).

[20] M. F. Hundley and J. C. Eckert (unpublished).

[21] F. J. Blatt and P. A. Schroeder, *Thermoelectricity in Metallic Conductors* (Plenum, New York, 1978).

[22] L. C. Bourne, K. Chang, M. L. Cohen, A. Stacy, and A. Zettl (unpublished).

[23] L. C. Bourne, A. Zettl, and A. Stacy (unpublished).

[24] N. P. Ong and P. Monceau, Solid State Commun. **26**, 487 (1978).

[25] Note that the Hall angle $\tan\theta = R_H \sigma H$, need not be zero in a superconductor since $\sigma \rightarrow \infty$ while $R_H \rightarrow 0$.

[26] For a review, see D. U. Gubser, T. L. Francavilla, S. A. Wolf, and J. R. Leibowitz, *Inhomogeneous Superconductors–1979* (AIP, New York, 1980).