Properties of $La_{1.8}Sr_{0.2}CuO_4$ superconductors

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(Received 3 February 1987; accepted for publication 20 February 1987)

Critical current, critical field, and carrier density measurements have been made on bulk samples of $La_{1.8}Sr_{0.2}CuO_4$ to assess the potential of such oxide superconductors for practical applications. The importance of preparing samples in a high oxygen pressure was documented. The upper critical field at $T = 0$ was estimated to be 530 kOe. From magnetization hysteresis loops, critical current densities were determined between 0 and 60 kOe. At 60 kOe, the values were 2×10^3 A/cm^2 at 4.2 K and 4×10^2 A/cm^2 at 18 K in samples that exhibited characteristics of weak flux pinning. The effective carrier density at 48 K was 1×10^{21} cm^{-3}, approximately half of the expected upper limit. A set of microscopic superconducting parameters has been derived from transition temperature, resistivity, and upper and lower critical field measurements made on a single specimen.

Ternary, mixed valence copper oxides of the type $(La,M)_nCuO_y$, where M = Ca, Sr, or Ba, $n = 1$, 3/2, or 2, and where the oxygen content, $y < 4$, shows the presence of oxygen defects (vacancies), were studied extensively by Michel, Raveau, and collaborators.[1] They observed that many such compounds exhibit a metallic behavior, dependent upon the M substitution and oxygen content. Bednorz and Mueller discovered high critical temperature superconductivity in La-Ba-Cu oxides and determined that the superconducting phase is $(La,Ba)_2CuO_4$ which crystallizes in the layered perovskite-type K_2NiF_4 structure.[2,3] Confirmation of superconductivity and the superconductivity phase identification were independently achieved at the University of Tokyo.[4–6] Indications of superconductivity, especially under pressure, were also reported by Chu *et al.*[7]

The Tokyo group found superconductivity also for M = Ca and Sr, $n = 2$. The Sr substitutions of $x = 0.15$–0.3 in $La_{2-x}Sr_xCuO_4$ resulted in very high critical temperatures T_c with onsets above 37 K.[8] Independently, "bulk superconductivity" at 36 K was observed in this compound ($x = 0.2$) by Cava *et al.* with onsets up to 52 K at other x values.[9] In this letter, we report on the Sr-substituted compound having $x = 0.2$ and concentrate on the determination of the upper critical field, carrier density, and critical current density, in order to fully characterize a single sample, and to assess the potential of such oxide superconductors for practical applications.

Samples were prepared from reagent grade La_2O_3, CuO, and $SrCO_3$ by mixing the constituents and reacting at 1000 °C for 16 h in oxygen. The reaction mixture was reground, the same heat treatment repeated, and the product reground again. The resulting powder was pressed into 1-mm-thick pellets and sintered at 1100 °C for 16 h. The pellets were cooled in flowing O_2 to 500 °C, where they were held for 4 h before cooling in O_2 to room temperature. The density of the pellets was between 5.85 and 6.00 g/cm^3, approximately 85% of the x-ray density. Data reported below refer to this material unless otherwise stated. One of the samples was in addition sequentially annealed at 500 °C, first in 150 bar of O_2 and later in Ar for 16 h each.

Bednorz and Mueller have suggested that the metallic behavior and, presumably, the superconductivity in these oxide compounds are related to the mixed valence of copper, co-present as Cu^{2+} and Cu^{3+} (Ref. 2). The Cu^{3+} ions can exist only if at least some of the substitution of Sr for La in the K_2NiF_4-type structure does not result in the creation of oxygen vacancies. The upper limit to the carrier density can be estimated by assuming total filling of oxygen vacancies. For $x = 0.2$, and assuming one carrier per Sr atom, the upper limit is 2.1×10^{21} cm^{-3}. Annealing at high oxygen pressure should maximize the carrier density and, probably, also the T_c.

The x-ray diffractometer trace of a powdered final sample is given in Fig. 1(a) and shows that the dominant phase had the tetragonal K_2NiF_4 structure [Fig. 1(b)], in agreement with Goodenough *et al.* who were the first to synthesize Sr-substituted La_2CuO_4.[10] A minute amount of a second phase corresponding to the orthorhombic La_2CuO_4 was also present,[11] as seen by comparing the trace of Fig. 1(a) with the reference trace of Fig. 1(c).

The dependence of resistance upon temperature was measured by the four-point van der Pauw method using a current density of ~1 A/cm^2. Between 0.2 and 2 A/cm^2, the current density did not affect the results. As a primary internal standard for temperature measurements, we used a Ge

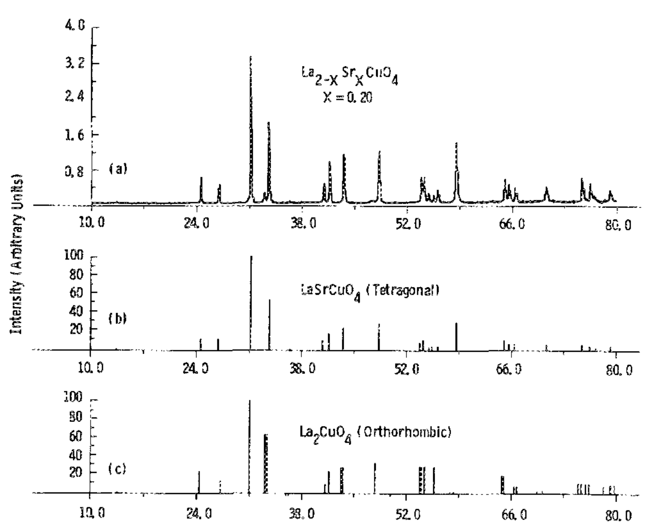

FIG. 1. Diffractometer trace of (a) a synthesized $La_{1.8}Sr_{0.2}CuO_4$ sample, (b) and (c) reference traces based on Refs. 10 and 11.

thermometer, Cryo-Cal CR500, calibrated by the manufacturer to an accuracy of ± 0.04 K. Other Ge and Pt resistance thermometers were calibrated by the standard and the samples were kept in thermal equilibrium with the thermometer to better than $\pm$ 0.5 K. Electrical contacts to samples were made with beryllium copper springs aided, in some cases, by silver paint or, for Hall constant measurements, by evaporated gold pads.

Table I shows room-temperature resistivity ρ_{300} and resistance ratio data. All samples showed metallic behavior. Resistance increased linearly with temperature above T_c and no localization effects were seen. After the high oxygen pressure treatment, ρ_{300}/ρ_{40} increased and T_c increased by at least 0.5 K. After the subsequent treatment in Ar, ρ_{300}/ρ_{40} decreased and the transition width broadened without fully reverting to properties prior to annealing. This shows that the oxygen "intercalated" into the vacancies at high pressure can remain there even under adverse conditions.

Figure 2 shows a typical superconducting transition. Samples fabricated by the same procedure had similar superconducting properties with transition onsets (5%) of 38–39.5 K and resistance equal to zero, within the accuracy of measurement, below 34–36 K. Transition widths, defined as 5 and 95% of the resistive transition, were between 4 and 5 K. The van der Pauw specimens also exhibited reproducible, sharp, minor resistance drops occurring between 55 and 71 K such as that shown in the insert of Fig. 2. These discontinuities could have been interpreted as possible signatures of some minor high-temperature superconducting phase. No such resistance drops, however, were seen in a narrow bar sample and we believe that they were simply caused by a redistribution of current in van der Pauw samples. The residual resistivity values of 350 to 550 $\mu\Omega$ cm were approximately a factor of 6 lower than in Ref. 9.

An estimate of the upper critical field at $T = 0$, $H_{c2}(0)$, was obtained from $dH_{c2}/dT = 21 \pm 1$ kOe/K near T_c. This value was determined from resistive transition midpoint values measured in magnetic fields up to 55 kOe. The estimate, $H_{c2}(0) \simeq 530$ kOe, was calculated in the dirty limit assuming zero paramagnetic limiting.[12]

Hall constant measurements were made by the standard dc technique using the van der Pauw configuration. The current density was at least 0.2 A/cm^2. At $T = 48$ K and $H = 50$ kOe, the measured Hall constant was $R_H = -(5 \pm 2) \times 10^{-3}$ cm^3/C. From this, an effective carrier density n^* was deduced from $n^* = (R_H e)^{-1} \simeq 1 \times 10^{21}$ cm^{-3}. The sign of the Hall constant indicated that the carriers are electrons. The magnitude of n^* was approximately 50% of the upper limit based on one carrier per Sr atom. This is similar to the carrier density in known perovskite superconductors of the type $BaPb_{1-x}Bi_xO_3$ (BPB).[13]

TABLE I. Results of annealing samples at 500 °C for 16 h in different atmospheres.

Annealing atmosphere	T_c (K) 5–95%	ρ_{300}/ρ_{40}	ρ_{300} ($\mu\Omega$ cm)
1 bar O_2	39.2–34.6	3.08	1370
150 bar O_2	39.5–35.6	4.06	1420
1 bar Ar	39.5–34.5	3.67	1320

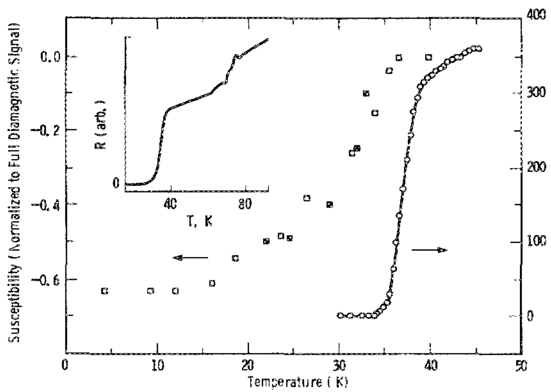

FIG. 2. Superconducting transitions from resistance (circles) and magnetic susceptibility (squares) measurements. The susceptibility is normalized to that of a bulk superconductor of the same volume and shape. Open squares were obtained by applying the field at the temperature of measurement. Full squares correspond to cooling in field through T_c. Insert shows a discontinuity in the resistance curve attributed to a possible current redistribution in van der Pauw measurements.

Magnetic moments in very low fields of 20–150 Oe and the moment hysteresis loops in fields up to 60 kOe were measured over the temperature range of interest using a vibrating sample magnetometer. From these data, the dc magnetic susceptibility and the critical current density were calculated, and the lower critical fields $H_{c1}(T)$ estimated.[14,15] The susceptibility versus temperature is plotted in Fig. 2. The diamagnetic signal was zero for $T > 40$ K and upon cooling appeared after the completion of the resistive transition. The ordinate was normalized to the diamagnetism of a bulk superconductor of identical shape and size. As in Ref. 9, at lower temperatures we obtained about 60% of full diamagnetism. The porosity of the measured sample (14%) was close to the percolation threshold. The strong diamagnetic signal, however, indicated that the threshold was not reached. The sample behaved as a bulk superconductor (however, see Ref. 14). While the transition temperature onset shown was close to that determined resistively, the transition width was much broader, thus clearly indicating that the measured sample was inhomogeneous with part of the volume having lower T_c's. Indeed, the $H_{c1}(T)$ estimated from low-temperature moment data extrapolated to zero at 21 K, with $dH_{c1}/dT = 7.9$ Oe/K.

Field dependences of the critical current density, $J_c(T)$, are shown in Fig. 3 for temperatures between 4.2 and 30 K. The level of J_c was low, between 10^3 and 10^4 A/cm^2 at 4.2 K. The temperature-dependent peak effect was an indication of the sample inhomogeneity and weak flux pinning. Another indication of inhomogeneity was that neither the low field J_c scaled with T^2 nor the high field J_c with T. The very gradual change of J_c versus the field intensity confirmed that at lower temperatures the upper critical fields were very high. Our J_c measurements have been performed on thin circular disks with demagnetization effects negligible above 10 kOe.[15] Comparisons of J_c's from magnetization data and from transport measurements were made on samples of other superconductors with similar or higher porosities. Good agreement was found. Based on such comparisons, the data of Fig. 3 are considered to be accurate within a factor of < 2, especially in higher fields.

From results of the type shown above, we estimated several pertinent parameters of the new superconductor. Mea-

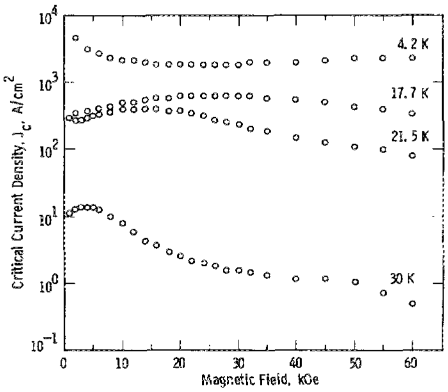

FIG. 3. Critical current density plotted as a function of magnetic field intensity. The data were obtained from magnetic moment hysteresis loops.

TABLE II. Material parameters either measured for one particular sample or derived from T_c, dH_{c2}/dT, ρ_{40}, and n.

Measured parameters			
Transition temperature midpoint	$T_c = 36.5$ K		
Normal-state resistivity	$\rho_{40} = 550\ \mu\Omega$ cm		
Upper critical field slope	$dH_{c2}/dT = 21 \pm 1$ kOe/K		
Lower critical field slope	$dH_{c1}/dT = 7.9 \pm 2.0$ Oe/K		
Effective carrier density	$n^* = 1\times10^{21}$ cm^{-3}		
Derived parameters			
Parameters	Calculated with $n = 10^{21}$	$\geq 10^{22}$	cm^{-3}
Electronic specific heat coefficient	$\gamma = 1.0$	2.7	mJ/K^2/mole
Ginzburg–Landau coherence length	$\xi(0) = 21$	21	Å
Ginzburg–Landau penetration depth	$\lambda(0) = 4100$	2500	Å
Ginzburg–Landau κ	$\kappa = 200$	120	
Thermodynamic critical field	$H_c(0) = 2.7$	4.5	kOe
Depairing critical current density	$J_d(0) = 5\times10^5$	1.4×10^6	A/cm^2

sured parameters for one particular sample are listed in Table II. The other parameters shown in Table II were calculated[16] from T_c, dH_{c2}/dT, ρ_{40}, and n without accounting for the facts that T_c and dH_{c2}/dT represented transition midpoints of the highest T_c fraction of inhomogeneous samples and ρ_{40} was an intergrain, rather than an intragrain, resistivity. Also listed in Table II are parameters calculated in the dirty superconductor limit to provide a comparison with Ref. 9 and to show the largest errors that could result if Hall measurements greatly underestimated the carrier density. The carrier density n would have to be greater than 10^{22} cm^{-3} for the dirty limiting form of the relations in Ref. 16 to be applicable.

The set of parameters was calculated a second time in the dirty limit using only those measured parameters that were likely to be independent of the coupling between grains: T_c, dH_{c2}/dT, and dH_{c1}/dT. The inferred parameters were within 25% of the values given in Table II (perhaps fortuitously, considering the low accuracy of H_{c1} determination), and suggested that the intragrain resistivity was 25% lower than the measured value. The inferred intragrain resistivity $\rho_{40} = 410\ \mu\Omega$ cm.

The value of γ in Table II, 2.7 mJ/K^2/mole = 850 erg/K^2/cm^3, was in good agreement with the value in Ref. 9 (calculated in the same way). However, the calculation based on $n = 10^{21}$ cm^{-3}, $\gamma = 1.0$ mJ/K^2/mole = 310 erg/K^2/cm^3, was rather low, comparable to values in BPB.[17] The coherence length and penetration depth were typical of an extreme type II superconductor, reminiscent of NbN. The depairing critical current, calculated following Ref. 18, was not prohibitively low for practical applications. We note that the measured J_c values, while low, were also similar to those in sintered NbN and clearly not optimized.[19] Electronic applications thus appear possible, assuming that films of the new superconductor family could be fabricated with a sufficient homogeneity and no surface decomposition due, for example, to the loss of oxygen. Prospects for application to large-scale conductors are less clear at this point. The microparticle technology of conductor fabrication might be considered as applicable if critical current density in homogeneous, optimized powder particles can be made high enough.[20]

The authors wish to acknowledge the assistance of A. M. Stewart with x-ray analysis and the encouragement of J. K. Hulm. Note: upon completion of work presented in this letter, we received a preprint by Tarascon *et al.* who investigated compositional dependences of superconductivity in Sr-substituted compounds.[21] The resistivity and T_c results for $x = 0.2$ are comparable. This work was supported in part by the Air Force of Scientific Research, contract No. F49620-85-C-0043.

[1] C. Michel and B. Raveau, Rev. Chim. Min. **21**, 407 (1984), and references therein.

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

[3] J. G. Bednorz, M. Takashige, and K. A. Mueller, Europhys. Lett. (to be published).

[4] S. Uchida, H. Takagi, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. Lett. (to be published).

[5] H. Takagi, S. Uchida, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. Lett. (to be published).

[6] S. Uchida, H. Takagi, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. Lett. (to be published).

[7] C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang, Phys. Rev. Lett. **58**, 405 (1987), and presentation at the 1986 MRS Fall Meeting, Symposium S, Boston, MA (unpublished).

[8] K. Kishio, K. Kitazawa, S. Kanbe, I. Yasuda, N. Sugii, H. Takagi, S. Uchida, K. Fueki, and S. Tanaka, Chem. Lett. (to be published).

[9] R. J. Cava, R. B. van Dover, B. Battlog, and E. A. Rietman, Phys. Rev. Lett. **58**, 408 (1987).

[10] J. B. Goodenough, G. Demazeau, M. Pouchard, and P. Hagenmuller, J. Solid State Chem. **8**, 325 (1973).

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

[12] N. R. Werthamer, E. Helfand, and P. C. Hohenberg, Phys. Rev. **147**, 295 (1966).

[13] T. D. Thanh, A. Koma, and S. Tanaka, Appl. Phys. **22**, 205 (1980).

[14] Since the sample vibrated in a magnetic field which, in our case, was not highly homogeneous, flux expulsion could not be observed, and the dc diamagnetic susceptibility so obtained could not be taken as a proof of superconductivity. In Fig. 2, no difference can be seen between susceptibility obtained when cooling through T_c in field and without the field applied. We assume that the superconducting origin of observed diamagnetic signals was sufficiently proven by others.

[15] M. R. Daniel and M. Ashkin, Cryogenics **10**, 610 (1976).

[16] Calculations based on the compilation of BCS relationships in T. P. Orlando, E. J. McNiff Jr., S. Foner, and M. R. Beasley, Phys. Rev. B **19**, 4545 (1979), with $S/S_F = 0.5$.

[17] B. Battlog, Physica B **126**, 275 (1984).

[18] H. London, Proc. R. Soc. A **152**, 650 (1935).

[19] N. Pessal, C. K. Jones, H. A. Johansen, and J. K. Hulm, Appl. Phys. Lett. **7**, 38 (1965).

[20] A. I. Braginski and A. T. Male, IEEE Trans. Magn. (to be published).

[21] J. M. Tarascon, L. H. Greene, W. R. McKinnon, G. W. Hull, and T. H. Geballe (Bell Communications Research Laboratory), to be published in Science.