PHYSICAL REVIEW B VOLUME 35, NUMBER 10 1 APRIL 1987

Magnetization of superconducting lanthanum copper oxides

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(Received 10 February 1987)

Magnetization studies of the high-transition-temperature lanthanum-copper-oxide superconductors have been carried out to determine the electromagnetic and flux-pining properties of these materials. Over much of the field-temperature plane the magnetization curves are highly reversible, which allows thermodynamic relations to be used to obtain an estimate of the free energy. The material appears to have a granular character and very low flux pinning.

INTRODUCTION

A new family of materials based on the lanthanum-copper-oxide system has been shown to have remarkably high superconducting transition temperatures.[1-5] The electrical resistance was observed[1] to drop by several orders of magnitude at temperatures above 30 K, and it was quickly established that there was Meissner screening arising from a phase having the K_2NiF_4-type crystal structure.[2,3] Many features of the upper critical field,[4,5] crystal structure, and phase diagram have been established.[2,6,7] In this Rapid Communication we report magnetization curves for these new materials. The data provide information about the free-energy difference between the superconducting and normal state over much of the magnetic-field-temperature (H-T) plane, and also provide a preliminary estimate of flux pinning. The goal of the work has been to determine some of the fundamental thermodynamic and transport properties that will be important in the application of these materials to microelectronic and magnet conductor applications.

EXPERIMENT

Samples were prepared by using high-purity Ames Laboratory powders La_2O_3, CuO, $BaCO_3$, BaO, SrO, and CaO. The predried powder mixtures were pressed into $\frac{3}{8}$ in. pellets of approximately 65% of the theoretical density and sintered in air at 1100 °C for two days in alumina crucibles. X-ray powder-diffraction patterns clearly show the formation of the tetragonal K_2NiF_4-type structure (space group $I4/mmm$) for the Sr compound and an orthorhombic modification (space group $Fmmm$) for the Ba and Ca compounds.[8] Lattice parameters were determined by the method of least squares using 14 (17) reflections for the tetragonal (orthorhombic) unit cell plus an internal silicon standard ($a = 0.543083$ nm). For the three samples in this study, we obtain the following: $(La_{1.85}Sr_{0.15})CuO_4$, $a = 0.3774(1)$ nm, $c = 1.3231(5)$ nm; $(La_{1.85}Ba_{0.15})CuO_4$, $a = 0.5352(4)$ nm, $b = 0.5385(4)$ nm, $c = 1.3253(7)$ nm; $(La_{1.85}Ca_{0.15})CuO_4$, $a = 0.5332(9)$ nm, $b = 0.5386(9)$ nm, $c = 1.3166(16)$ nm.

Resistivity data were taken with a standard four-probe technique with 0.002-in.-diam-Pt wires spot welded to a rectangular sample cut from the sintered pellet. Magnetization data were taken with a commercial SQUID magnetometer[9] in which the sample is moved slowly through the pick-up coil. Temperature was measured with carbon glass thermometers calibrated to an accuracy of 0.010 K.

RESULTS AND DISCUSSION

The onset of superconductivity in these samples was detected by measurements of both the electrical resistance and the magnetic moment arising from magnetic flux expulsion. Although we have done extensive measurements on all three systems (Ba, Sr, and Ca), most of the results reported in this paper are on the Sr system because of its higher transition temperature. Resistance measurements were performed on a sample 1.85-mm long, with cross-sectional dimensions of 1.96 and 0.84 mm. As shown by the open circles in Fig. 1, the electrical resistance at 10 mA measuring current breaks away from linear behavior at about 50 K and drops by four orders of magnitude in the temperature interval from 37 to 35 K. The measuring current of 10 mA and sample resistance of 5.7 mΩ at 40 K yield a normal current density of 0.63 A/cm^2 and a resis-

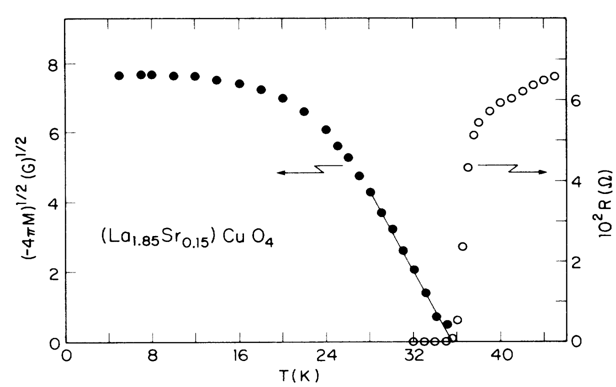

FIG. 1. Transition from the normal to superconducting state. Magnetization taken at $H = 100$ Oe.

tivity of 6000 $\mu\Omega$ cm for the sintered sample. No correction has been made for the porosity of the material.

Magnetization data[10] taken by cooling the sample in a magnetic field of 10 mT are shown by the solid circles of Fig. 1. The data are plotted as $(-4\pi M)^{1/2}$, since M is found to vary approximately as $(1-T/T_c)^2$ near T_c. As we show below, such a temperature dependence is to be expected for a material composed of phase-decoupled (or only very weakly Josephson-coupled) superconducting grains with linear dimensions comparable to the penetration depth $\lambda(T,H)$. Extrapolation of these data to $M=0$ yields $T_c=35.5$ K at $H=10$ mT.

At temperatures slightly below T_c, the 5.5-T magnet available with the SQUID magnetometer is sufficient to measure the entire magnetization curve. Hence, estimates of both the upper critical field H_{c2} and the thermodynamic critical field H_c can be obtained. Data for both 32 and 33 K are shown in Fig. 2. Since the lower critical field H_{c1} is 5 mT, it cannot be seen on this plot.

A remarkable feature of these data is the reversibility of the magnetization curves (Fig. 2). Data taken by sweeping the temperature give the same result as data taken by sweeping the magnetic field. To an accuracy of a few percent it does not matter whether the magnetic field is increasing (open symbols) or decreasing (solid symbols). Magnetic flux moves in or out of the sample with very little evidence of pinning. For applied fields less than about 0.1 T, however, values of $-4\pi M$ in decreasing field are less than in increasing field, as expected, but this effect is within the scatter of the data over most of the field range shown in Fig. 2.

An accurate determination of H_{c2} is complicated by the paramagnetism of these materials in the normal state.[11] The value of H_{c2}, however, can be conservatively estimated as the field where M reverses sign. These data then give an H_{c2} of 4.6 T at 32 K, 3.0 T at 33 K, and 1.3 T at 34 K. This gives a slope of $-dH_{c2}/dT=1.75$ T/K. Extrapolation to $T=0$ using the Werthamer-Helfand-Hohenberg theory[12] yields $H_{c2}\approx 43$ T.

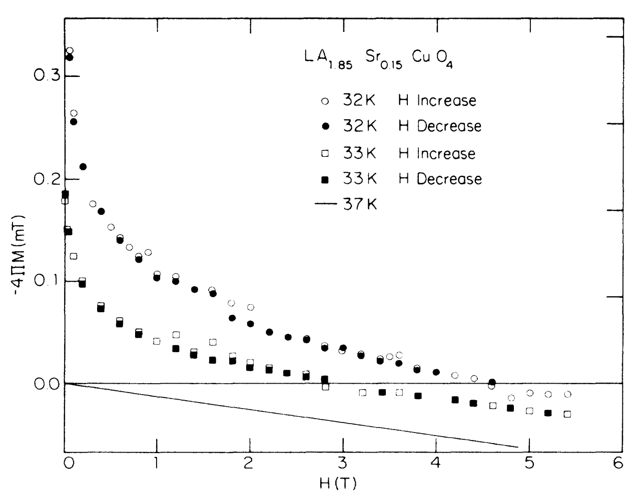

FIG. 2. Magnetization curves near T_c showing the degree of reversibility.

Experimental results for $-4\pi M$ in the Meissner state $(H<H_{c1})$ versus applied field H for the sample $(La_{1.85}Sr_{0.15})CuO_4$, shown in Fig. 3, exhibit a temperature-dependent slope. The offsets seen near $H=0$ are due to residual fields trapped when the current in the 5.5 T superconducting magnet is reduced to zero. Measurements in a copper magnet yielded the same slopes, but did not show these offsets. At $T=2$ K the initial slope $S=d(-4\pi M)/dH$ is abut 1.3, which is somewhat less than the value 1.5 expected for spherical particles with radii much larger than the penetration depth. As the temperature increases, S decreases, at first slowly, then more rapidly; S finally approaches zero linearly as T approaches T_c. At $T=30$ K, for example, $S\simeq 0.5$, and for $T/T_c > 0.85$, $S\simeq 4.41(1-T/T_c)$.

Such a temperature dependence of S follows from a description of the sample as an array of weakly coupled, roughly spherical superconducting grains whose average radius R is comparable with the penetration depth λ. As shown by London[13] in explaining magnetization experiments[14] on very fine-grained preparations of colloidal mercury, the theoretical initial slope is

$$S=d(-4\pi M)/dH=\tfrac{3}{2}P(R/\lambda) ,$$

where

$$P(x)=1-(3/x)\coth(x)+3/x^2$$

is a monotonically increasing function of x. Since λ increases with temperature and diverges as $\lambda=\lambda_0' \times(1-T/T_c)^{-1/2}$ at T_c, S decreases monotonically with T and approaches zero as $S=(R^2/10\lambda_0'^2)(1-T/T_c)$. This analysis, using data similar to that of Fig. 3, but at temperatures closer to T_c, gives R/λ_0' in the range 7–10.

Extension of London's method to the mixed state of the

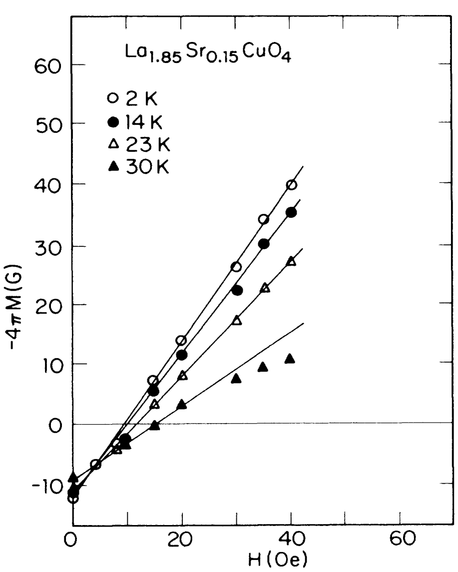

FIG. 3. Magnetization curves below H_{c1} showing the temperature dependence of the slope.

grains yields for the measured magnetization

$$-4\pi M(H)=[-4\pi M_0(H_{in})]3P(R/\lambda)/[2+P(R/\lambda)], \quad (1)$$

where $M_0(H_{in})$ is the equilibrium magnetization appropriate to a bulk cylindrical specimen in a parallel field, in which case the internal field H_{in} would be equal to the applied field. The penetration depth appearing in Eq. (1) is both temperature and field dependent;[15-18] near T_c,

$$\lambda(T,H)\simeq\lambda_0'(1-T/T_c)^{-1/2}(1-H/H_{c2})^{-1/2} .$$

Because of the factor in Eq. (1) involving $P(R/\lambda)$, the quantity H_c^* defined by the integral

$$H_c^{*2}/8\pi=-\int_0^{H_{c2}}MdH \quad (2)$$

is less than the bulk thermodynamic critical field H_c, which is defined by Eq. (2) with H_c^*, M and H replaced by H_c, M_0, and H_{in}. It is easily seen from Eqs. (1) and (2) that $H_c^*<H_c[3P_0/(2+P_0)]^{1/2}$, where $P_0(T)=P[R/\lambda(T,0)]$ can be obtained from measurements of $S(T)=d(-4\pi M)/dH$ in the Meissner state, in which $-4\pi M_0=H_{in}=(1+P_0/2)H$. Near T_c we may use the Abrikosov result[19]

$$-4\pi M_0(H_{in})=(H_{c2}-H_{in})/\beta_A(2\kappa^2-1) ,$$

where $\beta_A=1.1596$, to obtain from Eq. (1)

$$(-4\pi M)^{1/2}\simeq\frac{R}{\lambda_0'}\left[\frac{|dH_{c2}/dT|_{T_c}}{10\beta_A(2\kappa^2-1)T_c}\right]^{1/2}[T_c(H)-T] , \quad (3)$$

where $T_c(H)$ is the temperature at which $H=H_{c2}(T)$. From Eq. (3) and the data of Fig. 1 we obtain $\kappa\simeq50$.

To estimate H_c, we have first numerically integrated Eq. (2) up to the field H_{c2}, where M changes sign to obtain $H_c^*(T)=26.7$, 14.9, and 5.6 mT at $T=32$, 33, and 34 K, which yields the slope $[dH_c^*/dT]_{T_c}\simeq-11$ mT/K. Including the correction factor $[(2+P_0)/3P_0]^{1/2}$ obtained from measured values of $S(T)$ in the same range, we estimate the slope of H_c at T_c to be $[dH_c/dT]_{T_c}\simeq-14$ mT/K, which is comparable to that of ordinary superconductors such as Pb or Nb. Using the BCS result[20,21]

$$dH_c/dT|_{T_c}=-1.74H_c(0)/T_c$$

we thus estimate $H_c(0)\simeq0.3$ T. Combining the slopes of H_c and H_{c2} at T_c yields a second estimate of $\kappa\simeq90$. The zero-temperature values of the penetration depth, coherence length, and lower critical field are estimated, using dirty-limit theory,[22,23] to be $\lambda(0)\simeq330$ nm, $\xi(0)\simeq3.0$ nm, and $H_{c1}(0)\approx5.2$ mT. The average radius of a superconducting grain is thus calculated to be in the range 1.3–2.0 μm. Using the formula[22,23] $\gamma=0.0558(dH_c/dT)^2_{T_c}$, we obtain $\gamma=0.11$ mJ/cm^{3}K^2 compared with $\gamma=0.16$ mJ/cm^{3}K^2 for Pb (Ref. 24). From the expression $\gamma=(2\pi^2/3)N(0)k_B^2$ and the unit cell volume $a^2c=1.88\times10^{-22}$ cm^3 we obtain $N(0)=2.7$ states-eV-unit cell. For the jump in specific heat at T_c, the data predict

$$C_s-C_n=(T_c/4\pi)(dH_c/dT)^2_{T_c}=5.5 \text{ mJ/cm}^3\text{K} .$$

The above values of $[dH_{c2}/dT]T_c$ and γ yield[25] a normal-state resistivity of $\rho_n\approx350$ $\mu\Omega$ cm for the superconducting grains. This suggests that the measured resistivity of 6000 $\mu\Omega$ cm just above T_c is dominated by high-resistivity material separating the superconducting grains. Below T_c of the superconducting grains, the high resistivity material can carry only weak Josephson currents ($\sim10^2$ A/cm^2).

In addition to the study of the Sr compound described above, a fairly complete study also has been made of a powder sample of $(La_{1.85}Ba_{0.15})CuO_4$ with a T_c of 32.5 K. The Ba sample is very similar to the Sr sample in that the magnetization curves are reversible, the slope of the magnetization below H_{c1} falls with increasing temperature, and there is very little flux pinning for magnetic fields above 20 mT. A $(La_{1.85}Ca_{0.15})CuO_4$ sample showed a T_c of 21 K. An extensive study of this material will be reported elsewhere.

CONCLUSION

The pressed pellet samples of $(La_{1.85}Sr_{0.15})CuO_4$ are well behaved high-κ superconductors with a free-energy difference between the superconducting and normal states comparable to that of Pb or Nb. Magnetization curves are reversible over large portions of the H-T plane, indicating very low pinning. Values of H_{c2} determined from flux exclusion near T_c indicate a low-temperature upper-critical field on the order of 40 T. Moreover, the magnetization data appear to be well described by modeling the material as an array of relatively small superconducting grains that are very weakly Josephson coupled. This granular nature may be a consequence of the sample preparation technique and may not necessarily represent an inherent material property. The granular character of the material, the high T_c, and the rather low-flux pinning make this material attractive for microelectronic applications. The preparation of high-critical-current conductor material, however, offers a substantial challenge.

ACKNOWLEDGMENTS

We would like to thank many authors for providing preprints. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-ENG-82. This work was supported by the Director for Energy Research, Office of Basic Energy Sciences.

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