Phase separation in a high-pressure-oxygenated $La_2CuO_{4+\delta}$ crystal: Evidence from anisotropic electronic transport and magnetic susceptibility

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(Received 30 October 1989)

We report magnetic susceptibility, resistivity, and thermoelectric power measurements performed on a high-pressure-oxygenated $La_2CuO_{4+\delta}$ single crystal. Distinct anomalies are present in all three quantities between 200 and 280 K that are attributed to a phase separation involving oxygen diffusion. Hysteresis present in the data near the phase-separation temperature indicates that the process is weakly first order. We suggest that this transition may be driven, in part, by interactions between excess oxygen ions and copper spin magnetism.

$La_2CuO_{4+\delta}$ is the parent compound to the hole-doped cuprate superconductors with transitions near or below 40 K.[1] This compound has been studied extensively because it embodies much of the physics and chemistry generic to the high-temperature conductors. For $\delta=0$, $La_2CuO_{4+\delta}$ is a Mott insulator in which the copper moments undergo three-dimensional antiferromagnetic ordering at $T_N \approx 325$ K.[2,3] By adding excess oxygen ($\delta>0$) the material becomes hole doped. This acts to both reduce the Néel temperature and induce superconductivity below 40 K.[3,4] Early studies on extreme hole doping by way of high-pressure oxygenation of powder samples suggested that the excess oxygen went into the crystal structure in the form of a superoxide with $\delta=0.13$.[5] However, this value for δ is thought to have been influenced by unincorporated surface oxygen.[6] Refinement of a high-pressure-oxygenated single-crystal's neutron-diffraction spectra indicates that δ is 0.032.[7] Further, temperature-dependent neutron-diffraction work indicates that a reversible phase separation into two crystallographically distinct structures occurs near 320 K in oxygen loaded $La_2CuO_{4+\delta}$ powder samples.[8] Below the phase-separation temperature, the material is composed of both a nonsuperconducting, oxygen-poor ($\delta\approx 0$) phase with an orthorombic structure, and a superconducting, oxygen-rich ($\delta>0$) phase with a closely related orthorhombic structure. Single-crystal diffraction studies confirm this phase separation, but suggest that the separation occurs near 280 K.[9] Both poweder and single-crystal diffraction measurements indicate that the nonsuperconducting volume fraction is approximately $\frac{2}{3}$.[8,9] Muon-spin-rotation/relaxation experiments yield a similar value for this volume ratio.[10]

The electronic transport and magnetic properties of oxygen-loaded $La_2CuO_{4+\delta}$ might be expected to differ substantially from the well-documented[4,11,12] behavior of as-prepared or oxygen-reduced samples. In particular, one might anticipate anomalies in these properties near the phase-separation temperature. To investigate these possibilities we have measured the anisotropic resistivity, thermoelectric power, and magnetic susceptibility in a single crystal of high-pressure oxygenated (and superconducting) $La_2CuO_{4+\delta}$. Large anomalies are present in all three measured quantities in the temperature range 200–300 K. These results can be interpreted as arising from phase separation into a highly resistive oxygen-poor phase and a less resistive oxygen-rich phase.

$La_2CuO_{4+\delta}$ single crystals were grown from a CuO-rich La_2O_3-CuO melt in a platinum crucible. After quenching from high temperature, the sample was then given a post-synthesis anneal for 12 h at 575 °C in a 3 kbar oxygen atmosphere, followed by a 100 °C/h cool down.[8] Since the crystal was prepared under the same conditions as those used for the neutron-diffraction studies,[7,9] we assume that the average oxygen stoichiometry is 4.032 and the phase-separation temperature is roughly 280 K.

Magnetic susceptibility measurements were performed with a Quantum Design SQUID magnetometer. Magnetization measurements in a 20 G magnetic field showed $100\pm10\%$ of perfect flux shielding at 5 K, with a superconducting onset temperature of 35 ± 1 K and a midpoint of 30 ± 1 K. In spite of the large flux shielding, the maximum Meissner effect in a 20 G field was only a few percent of $-1/4\pi$. Figure 1 shows the out-of-plane magnetic susceptibility in a 5 kG magnetic field in the nonsuperconducting temperature region ($T>40$ K); the in-plane susceptibility (not shown) is qualitatively similar to the data shown in Fig. 1. The most striking feature of the data is the hysteretic bump located in the temperature range from 200 to 300 K. This feature is superimposed on a Pauli-like temperature-independent paramagnetic background. Although the susceptibility anomaly is far smaller, broader, and of a different character than that present[4] in antiferromagnetically ordered $La_2CuO_{4+\delta}$ ($\delta\approx 0$), its present suggests that some magnetic change occurs upon the onset of phase separation. As indicated by the warming and cooling arrows in Fig. 1, hysteresis [a

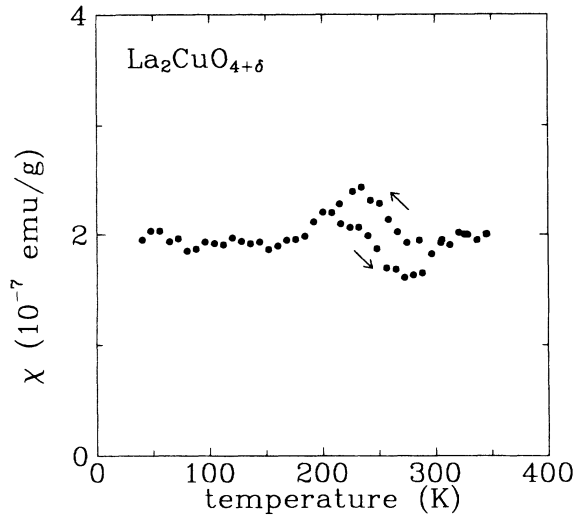

FIG. 1. Magnetic susceptibility of oxygen-loaded $La_2CuO_{4+\delta}$ plotted vs temperature. The susceptibility was measured in a 5 kG magnetic field directed perpendicularly to the copper-oxygen planes.

portion (10 K) of the 30 K hysteresis is attributed to nonequilibrium problems with the magnetometer] is evident in the magnetic anomaly which is not present at T_N in La_2CuO_4. Further, no evidence for a metamagnetic transition could be found in the oxygen-loaded crystal.

The anisotropic electrical resistivity was measured by a conventional four-probe ac technique. Silver conductive paint was used to make electrical contacts to the single crystal (contact resistances were typically 2Ω). Figure 2 depicts the resistivities both in and perpendicular to the copper-oxygen planes. The resistivity is highly anisotropic, with the (tetragonal) *c*-axis resistivity being roughly three orders of magnitude greater than that in the *ab* plane. As with the magnetic susceptibility, the in-plane resistivity shows a large and abrupt change beginning at the 280 K phase separation temperature. Between 280 and 200 K the slope of the in-plane resistivity doubles. Below 40 K the resistivity shows an abrupt transition to the superconducting ground state. Like the typical resistivities exhibited by most high-T_c superconductors, the in-plane resistivity is highly linear outside of the anomalous region in oxygen-loaded $La_2CuO_{4+\delta}$. As in carefully oxygenated T^* superconductors,[13] the data presented in Fig. 2 suggest that linear resistance versus temperature profiles in high-T_c compounds may be routinely observable given sufficient oxygen loading (hole doping).

The *c*-axis resistivity is also shown in Fig. 2 The *c*-axis resistivity is nearly temperature-independent above 100 K, and shows only a gradual rise below 100 K. Unlike the *ab*-plane data, the out-of-plane resistivity shows only a relatively tiny (2%) drop upon cooling through the phase-separation temperature. The superconducting transition is evident below 40 K in the *c*-axis data, but the resistance only drops by roughly 25%. This indicates that a complete superconducting path does not exist along the *c*-axis direction.

The thermoelectric power (TEP) was measured by using a standard technique[14] that employed a maximum relative temperature gradient of 1%. The in-plane TEP is depicted in Fig. 3. The TEP is positive at all temperatures, indicative of hole-like transport. As with the other data, the TEP shows a significant drop in value upon cooling through the phase-separation temperature. Outside the anomalous region (200 to 280 K), oxygen-loaded $La_2CuO_{4+\delta}$ displays a TEP that is similar to that found in most other lanthanum-cuprate-based materials,[4,13,15] namely a high-temperature plateau and a gradual reduction towards zero upon cooling below 200 K. Between 280 and 200 K the action of the phase separation appears to shift the TEP downward by roughly 25 μV/K. As with the in-plane resistivity, the planar thermopower drops abruptly to zero upon cooling below T_c.

Figure 4 shows an expanded view of the in-plane resistivity and thermoelectric power for the oxygen-loaded $La_2CuO_{4+\delta}$ crystal. Both quantities exhibit clear signs of hysteresis upon warming and cooling; although not shown in Fig. 4, hysteresis was also found in the *c*-axis

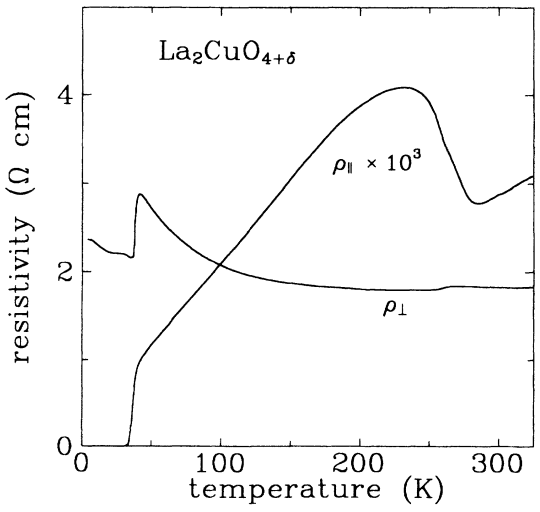

FIG. 2. Temperature dependence of the in-plane and out-of-plane resistivities of high-pressure oxygenated $La_2CuO_{4+\delta}$.

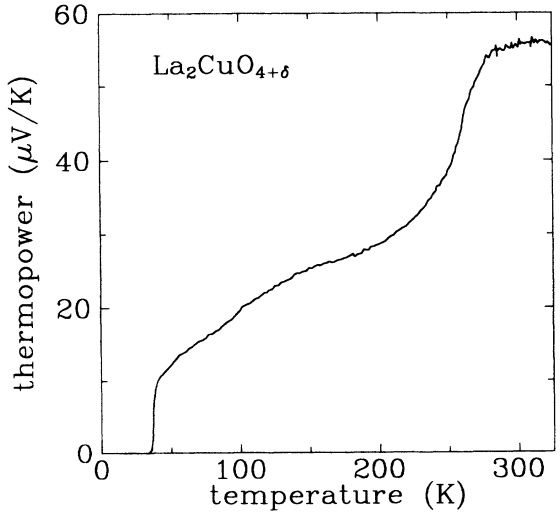

FIG. 3. In-plane thermoelectric power of an oxygen-loaded $La_2CuO_{4+\delta}$ crystal as a function of temperature.

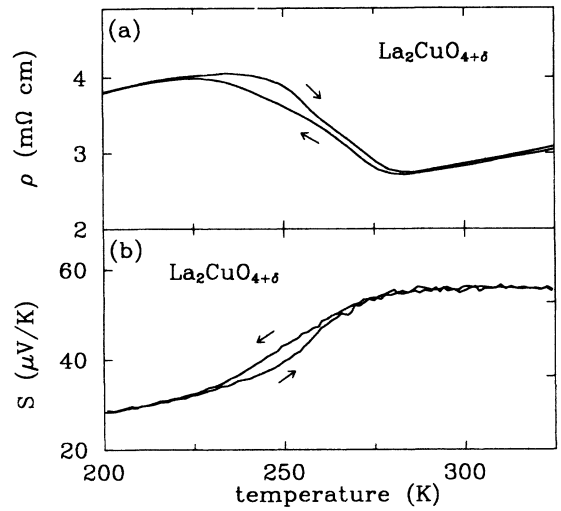

FIG. 4. In-plane resistivity (a) and thermoelectric power (b) of a high-pressure-oxygenated $La_2CuO_{4+\delta}$ crystal measured upon cooling and warming through the phase-separation temperature.

resistivity. These measurements were carried out through a number of thermal cycles and the data were reproducible in all cases. The presence of hysteresis in all three measured quantities demonstrates that the phase-separation process is at least weakly first order.

The overall features of both the resistivity and the thermoelectric power can be accounted for by a phase-separation "transition" near $T_{ps}=280$ K. Neutron-diffraction work[9] indicates that the excess oxygen is uniformly distributed in $La_2CuO_{4+\delta}$ for $T>T_{ps}$. The temperature-independent TEP and the linear-in-temperature in-plane resistivity indicate that the hole carriers conduct via either a weakly localized[16] or narrow-band[17] mechanism in this high-temperature, mixed state. At and below T_{ps} the excess oxygen ions diffuse to form oxygen-poor (O-poor) regions ($\delta\approx 0$) and oxygen-rich (O-rich) regions ($\delta>0.032$). The O-poor regions presumably act like nitrogen-annealed ($\delta=0$) $La_2CuO_{4+\delta}$ and may be responsible for the anomaly in the magnetic susceptibility. This O-poor phase should be highly resistive.[4] The O-rich phase, with its increase in oxygen and hence hole carriers relative to the $T>T_{ps}$ state, should be highly conductive. This is the phase responsible for the superconducting transition.

At T_c, the c-axis resistivity drops by only 25%, whereas the ab-plane resistivity goes completely to zero. This indicates that a complete superconducting path (i.e., through O-rich regions) does not exist along the crystal in the c-axis direction. This partial superconductivity along the c-axis gives compelling evidence that the two low-temperature phases are arranged as ab-planar domains which alternate along the c axis with a relative cross-sectional ratio (poor to rich) of roughly 3:1, qualitatively consistent with structural results (this cross-sectional ratio is expected to be strongly sample dependent owing to sample-to-sample variations in the high-pressure-oxygenation process). With regard to in-plane transport, a parallel alignment of domains mean that the insulating O-poor phase will be "shorted out" by the highly conducting O-rich phase as the phase separation develops. Hence, below T_{ps} both the in-plane resistivity and TEP predominately reflect transport in the O-rich phase. The large decrease in the effective conducting cross section is not sufficiently compensated by the increase in carriers in the O-rich phase, resulting in a doubling of the overall resistivity during the phase-separation process. The TEP, which is not sample-volume dependent, drops by 25 μV/K due presumably to an increase in the carrier concentration in the O-rich phase (the TEP of a narrow-band or weakly localized mechanism decreases with increasing carrier concentration).[16,17] Below 200 K the transport data display conventional behavior, indicating that the phase-separation process is complete below this temperature. The absence of any significant variation in the c-axis resistivity near T_{ps} indicates that the c-axis transport is for the most part left unaffected by the phase-separation process, although the change in resistivity in both directions is comparable.

With $\delta=0.032$, and assuming that the excess oxygen is uniformly incorporated throughout the material for $T>T_{ps}$ (neutron work[7-9] suggests that this may be the case), roughly one in 16 cells will contain an extra oxygen atom for $T>T_{ps}$. With $\delta\approx 0$ in the O-poor phase and a poor-to-rich volume ratio of 3 (as suggested by the c-axis resistivity data), excess oxygen conservation requires $\delta\approx 0.1$ in the O-rich phase, or one extra oxygen ion for every five unit cells. Hence, at T_{ps} the excess oxygen must diffuse to preferentially form areas of closely spaced "La_2CuO_5" cells (a similar process may be involved in air annealed $La_2CuO_{4+\delta}$ where large transport anomalies[4] occur at T_N). Given the anomaly present in the susceptibility data, the copper moments left in the O-poor regions appear to undergo some degree of magnetic ordering. This oxygen diffusion process appears to be completely reversible given that the transport data were entirely reproducible from cycle to cycle.

In closing, we briefly consider the possible driving force behind the reversible phase-separation process. The hysteresis evident in the data presented in both Figs. 1 and 4 indicates that the process is slightly first order in nature. It is well known that magnetoelastic coupling effects can give rise to a first-order transition.[18] Furthermore, preliminary nuclear magnetic resonance results indicate the *discontinuous* onset of magnetic order near T_p.[19] Hence, the reversible oxygen diffusion could be driven at least partially by magnetic fluctuations involving copper moments. The phase-separation process may, therefore, be a further manifestation of the close connection between electronic transport and magnetism in the high-T_c compounds.

ACKNOWLEDGMENTS

We thank M. C. Aronson and P. C. Hammel for useful discussions. Work at Los Alamos was performed under the auspices of the United States Department of Energy, Office of Basic Energy Sciences, Division of Materials Science. Work at Sandia National Laboratory was supported by the United States Department of Energy under Contract No. DE-AC04-76DP00789.

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