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Pressure dependence of the superconducting and Néel temperatures in a $La_2CuO_{4+\delta}$ crystal

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We have measured the temperature dependence of the resistance for a $La_2CuO_{4+\delta}$ single crystal at pressures from 1 bar to 18 kbar. The effects of pressure on the antiferromagnetic transition temperature T_N and the superconducting transition temperature T_c are compared to those of oxygen doping.

I. INTRODUCTION

As a result of its relationship to the 40-K $La_{2-x}(Sr,Ba,Ca)_xCuO_4$ family of superconductors,[1] $La_2CuO_{4+\delta}$ has attracted much experimental and theoretical interest. In particular, it has been found that the low-temperature state is extremely sensitive to δ, the deviation from half-band filling. Assuming a perfect La-to-Cu ratio of 2.0 $La_2CuO_{4+\delta}$ is a high-temperature antiferromagnet for small positive δ,[2] but a 40-K superconductor for $\delta = 0.13$.[3] At present, it is not clear for what range of δ superconductivity exists, or how the superconducting state develops from the antiferromagnetic state as δ is increased. Obtaining detailed information on the δ dependence of the Néel and superconducting temperatures is complicated not only by the difficulties of preparing samples with a continuous variation of oxygen stoichiometry, but also by the problem of distinguishing disorder effects from chemical alteration of the Fermi surface. Application of pressure can be illuminating in both respects. First, a rather large range of phase space may be explored by applying pressure to a sample of fixed δ, if the superconducting and Néel temperatures are pressure dependent. Second, since pressure reduces the unit-cell volume and modifies the Fermi level, variations of both the Fermi surface and interactions can be achieved without introducing additional disorder. Accordingly, we report here the pressure dependence of the superconducting and antiferromagnetic transition temperatures in a single crystal of $La_2CuO_{4+\delta}$.

II. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The measurements reported in this paper were performed on a single crystal of $La_2CuO_{4+\delta}$, grown from CuO flux. The crystal was then heated to 650 °C in air, after which the temperature was decreased to 200 °C over a period of 10 h before a final quench. X-ray-diffraction measurements on samples grown under similar conditions confirmed that the sample was single phase; the refinement analysis was optimized with a La:Cu ratio of 2.00 ± 0.02.

Electrical leads were attached to the sample with silver-filled epoxy in a four-probe configuration. The sample was pressurized in a self-clamping Be-Cu cell[4] using a 1:1 mixture of pentane and isoamyl alcohol as the hydrostatic pressure medium. The pressure was determined using a Pb manometer.

III. EXPERIMENTAL RESULTS

Magnetization measurements show that the sample has an antiferromagnetic anomaly at 257 K, with a steady decrease in susceptibility above the onset of diamagnetism at the superconducting transition temperature of 37 K. Meissner-effect measurements indicate that the superconductivity is limited to only a few percent of the sample volume. In addition, we find that when we abrade the surface layer of the crystal, the superconducting volume drops markedly. It is then reasonable to conclude that the oxygen concentration is not uniform in the sample: instead, the sample has an oxygen-rich surface layer of superconducting material and a more poorly oxygenated antiferromagnetic core. Bulk Hall-effect measurements given an oxygen concentration of 0.01 holes per unit cell, indicating that the antiferromagnetic core has a composition $La_2CuO_{4.0025}$. However, we presume that the small superconducting fraction has a composition near $La_2CuO_{4.13}$, as found by Schirber *et al.*[3] in high-pressure oxygenated superconducting samples.

Both these regions are evident in Fig. 1, depicting the temperature-dependent four-probe resistance, measured with both the voltage and current leads placed across the CuO planes. As will be reported in more detail elsewhere,[5] the perpendicular resistance initially increases with decreasing temperature before dropping off by a factor of $\frac{2}{3}$ below 270 K. The magnitude of this resistance drop is quite remarkable, far larger than expected from the usual loss of spin-disorder scattering at an antiferromagnetic transition. We take this as an indication that the carriers and the ordering moments are strongly coupled. We identify the Néel temperature T_N taken from the maximum in the temperature derivative of the magnetic susceptibility with the temperature at which the temperature derivative of the resistance is a maximum. At lower temperatures the resistance levels off before rising more gradually to the final superconducting drop at 37 K.

An interesting feature of the resistance is the observation of a pronounced temperature hysteresis near T_N, shown in the inset of Fig. 1. As the sample is temperature

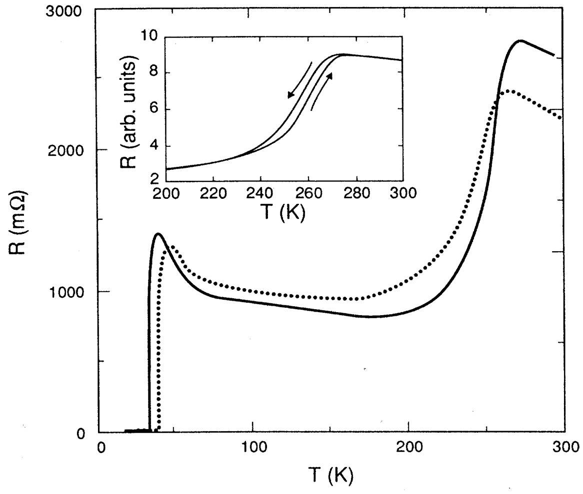

FIG. 1. Temperature dependence of the resistance at 1 bar (solid line) and 18 kbar (dotted line). Both are cooling curves. The inset shows the thermal hysteresis at 1 bar. The heating curve lies on the high-temperature side of the cooling curve.

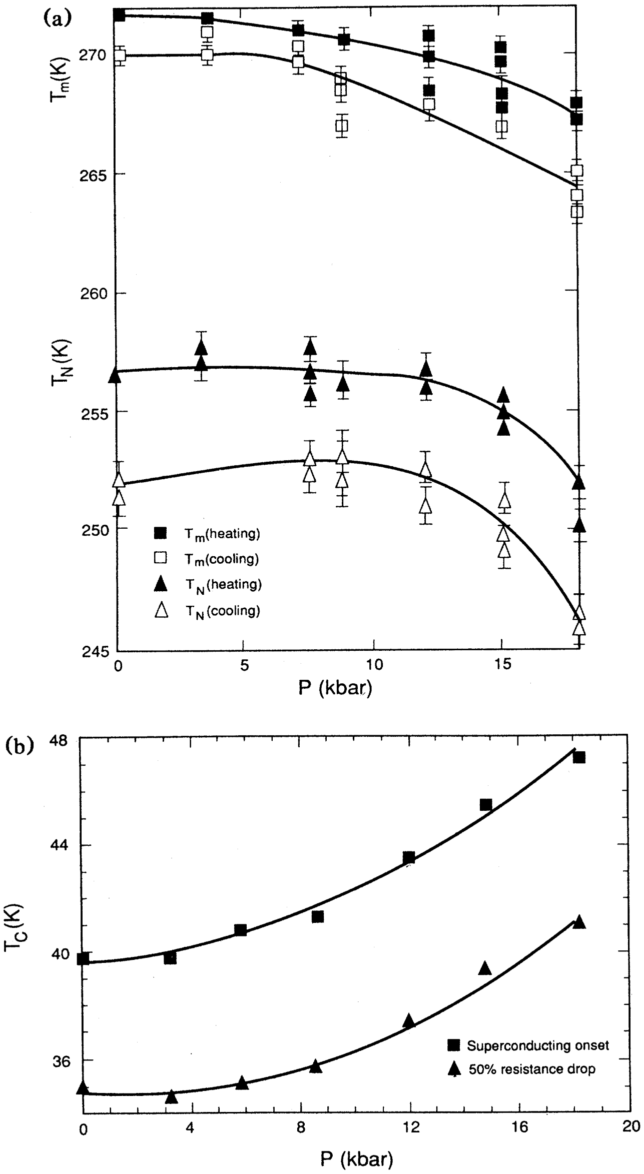

FIG. 2. (a) Pressure dependence of the resistance maximum T_m (squares) and the maximum temperature derivative of the resistance T_N (triangles). Cooling data are open symbols, while heating data are solid symbols. (b) Pressure dependence of the superconducting onset (squares) and 50% resistance drop (triangles). Lines are guides for the eye.

cycled, the heating curve consistently falls on the high-temperature side of the cooling curve. This result is independent of both the measuring current and the heating or cooling rate. In an effort to distinguish between metastable behavior and the hysteresis associated with a first-order phase transition, we have searched for a similar hysteresis in the magnetic susceptibility. Although no hysteresis greater than the experimental accuracy of 0.5 K was observed, it must be pointed out that we cannot be sure that the sample is in the same state for the zero-field resistance measurements and the 9-kOe field used in the magnetization measurement. Because of signal sensitivity conditions imposed by the small sample size, it was not possible to directly check for hysteresis in the magnetic susceptibility for fields less than 9 kOe. Additionally, detailed measurements of the specific heat using differential scanning calorimetry with a resolution of better than $0.1R\ln 2$ failed to reveal the pronounced anomaly reported by Jing, Zhao, and Qi-Ze.[6] Although we cannot entirely rule out the presence of a first-order phase transition, these results favor the interpretation of the hysteresis as the result of metastable behavior. It is possible that the carriers are pinned or preferentially scattered by metastable twin configurations in the sample. If this is so, it is puzzling that the hysteresis does not persist away from the Néel transition.

The temperature dependence of the resistance at 1 bar and 18 kbar is reproduced in Fig. 1. Although the qualitative features are unchanged, pressure decreases both T_N and the resistance drop associated with the transition. In addition, pressure increases T_c, an almost ubiquitous feature of the high-T_c materials. The pressure dependence of the temperature of the resistance maximum and of T_N for heating and cooling are plotted in Fig. 2(a). We note that the magnitude of the hysteresis is essentially unchanged with pressure. The temperatures of the superconducting onset and 50% resistance drop from 1 bar to 18 kbar are plotted in Fig. 2(b). Neither the superconducting nor antiferromagnetic transitions are appreciably broadened by pressure, indicating the absence of significant internal strains.

As previously observed in a polycrystalline La-deficient sample,[7] we find that T_N decreases only slightly below 10 kbar before dropping more rapidly at higher pressures. This result is in disagreement with those of Kaneko *et al.*[8] and Fujita *et al.*[9] These groups found, respectively, a linear increase and decrease of T_N with pressure. However, since both groups reported on polycrystalline samples without clearly defined antiferromagnetic resistance anomalies, their definitions of T_N are questionable. We suggest that in lieu of single-crystal work in which the antiferromagnetic anomaly is obvious, correlation of the resistance results to a more sensitive measurement, such as magnetic susceptibility, is indispensable.

IV. DISCUSSION

Several authors[8,10,11] have suggested that the antiferromagnetism of La_2CuO_4 results primarily from a superexchange interaction between Cu^{2+} ions. If the kinetic part of the superexchange interaction J dominates, then $J \sim zt^2/U$, with z the number of nearest neighbor magnetic ions, t the transfer integral, and U the intra-atomic Coulomb repulsion. With these assumptions, the pressure dependence of T_N is given by[12]

$$\frac{\partial T_N}{\partial P} = \frac{10}{3}\frac{T_N}{B}, \tag{1}$$

where B is the bulk modulus. This relationship is upheld for a number of garnets and ferrites. However, some skepticism should accompany the association of La_2CuO_4 with the simpler antiferromagnets. Cyrot[11] made the further proposal that if the superconductivity were mediated by antiferromagnetic spin fluctuations then T_c and T_N would both satisfy

$$\frac{\partial T_N}{\partial P} = \frac{10}{3}\frac{T_N}{B}$$

and (2)

$$\frac{\partial T_c}{\partial P} = \frac{10}{3}\frac{T_c}{B}.$$

Although this claim was initially substantiated by the results of Kaneko,[8] the current results are clearly inconsistent with this interpretation, since the pressure derivatives of T_N and T_c are pressure dependent and of opposite signs. It is also interesting to note that the antiferromagnetic transition does not appear to satisfy the Ehrenfest relation

$$\frac{1}{T_N}\frac{\partial T_N}{\partial P} \propto \frac{\Delta\alpha}{\Delta C_P}, \tag{3}$$

since it is found[13] that the in-plane thermal expansion anomaly $\Delta\alpha$ is positive near T_N. Recall that our specific-heat measurements revealed no anomaly near T_N; if measurable, the specific-heat jump ΔC_p would presumably be positive.

Our pressure measurements indicate that excess oxygen in $La_2CuO_{4+\delta}$ is analogous to a positive chemical pressure in the sense that T_N is reduced and T_c enhanced either by adding oxygen or applying pressure. Additional evidence for this equivalence is found from the magnetization measurements of Cheong, Thompson, and Fisk.[14] These workers find that, in air- and nitrogen-annealed single crystals with different T_N, the critical field H_c required to induce a metamagnetic transition scales with T_N. Using a classical spin model, they further propose that θ, the spin cant angle, is related to $H_c(\mathrm{O})$ through

$$J_\perp \sim \theta H_c(\mathrm{O}), \tag{4}$$

where $J_\perp$ is the interlayer exchange coupling. Most intriguingly, they also find that pressure decreases H_c at a rate compatible with the pressure reduction of T_N reported here. Taken together, these observations reinforce the similarities of pressure and oxygen doping, and suggest that their net effect is to decrease the crystallographic orthorhombicity. This conclusion is supported by x-ray scattering studies[15] which show that tetragonality is favored with pressure. Similarly, Johnston and coworkers[2] find that the Néel temperature and the orthorhombic transition temperatures scale together, and are reduced by oxygen doping. Neutron scattering measurements[16] provide a more detailed description of the tendency towards tetragonality observed with oxygen doping. Namely, the rigid tilt of the CuO_6 octahedra in the more highly oxygenated superconducting phase is distorted in random directions, leading to an overall lower spin cant θ, relative to nonsuperconducting samples.

We suggest that the decreased orthorhombicity observed with oxygenation and pressure results in more poorly coupled CuO planes. In this scenario, the interlayer exchange strength $J_\perp$ decreases more quickly than the intralayer exchange strength $J_\parallel$ changes, leading to the observed decrease in T_N with oxygenation. As magnetic decoupling of the planes increases with oxygenation or pressure, superconductivity is stabilized at the expense of the antiferromagnetism.

V. CONCLUSION

We have measured the pressure dependence of the resistance of a $La_2CuO_{4+\delta}$ single crystal prepared in CuO flux. Both surface superconductivity and bulk antiferromagnetism are observed in the sample. Here, the application of pressure plays a role analogous to the addition of oxygen, decreasing the Néel temperature and increasing the superconducting transition temperature. By comparing these results to those of magnetization, x-ray, and neutron scattering studies, we suggest that both pressure and oxygen doping magnetically decouple the CuO planes.

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