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Transport in crystalline $La_2CuO_{4+\delta}$: Enormous anomalies at T_N for small hole doping

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The anisotropic electrical resistivity ρ and thermoelectric power S have been determined on single crystals of $La_2CuO_{4+\delta}$ in which the hole doping δ has been varied by controlled anneals. An enormous decrease and hysteresis in both ρ and S occur at the Néel temperature T_N for small δ, suggesting strong coupling between magnetic order and transport. Possible origins of these transport anomalies are discussed.

Magnetic-susceptibility χ measurements on insulating $La_2CuO_{4+\delta}$, $\delta \simeq 0$, show evidence for both three-dimensional (3D) antiferromagnetic order[1,2] at T_N and a positive $d\chi/dT$ (Ref. 2) for temperatures well above T_N, a characteristic of 2D short-range antiferromagnetic order. Indeed, neutron scattering experiments[3] on La_2CuO_4 have established the existence of instantaneous spin correlations at temperatures far above T_N. Further, it appears from two-magnon Raman scattering[4] that the copper spins are coupled rather strongly, with the 2D magnetic exchange being on the order of 1400 K. When La_2CuO_4 is hole doped by substituting strontium for lanthanum, it becomes metalliclike and superconducting. X-ray absorption[5] suggests that these holes reside primarily on the oxygen sites but that there are still well-defined Cu^{2+} spins. Inelastic neutron scattering[6] on superconducting $La_{2-x}Sr_xCuO_4$ crystals (with $T_c \simeq 10$ K) also indicates that Cu^{2+} ions retain their spin but the mobile holes limit the spin-correlation length such that long-range antiferromagnetic order is not possible. One, however, must be careful when considering these results since T_c of this crystal is much lower than found on sintered materials of the same nominal stoichiometry. From Hall-effect measurements,[7] it is known that the linear relationship between hole concentration and strontium content breaks down for $x \gtrsim 0.1$ so that the importance of spin correlations for superconductivity is not totally clear. To understand the principal interactions necessary for high-temperature superconductivity, it seems essential to establish an accurate picture of the physics in $La_2CuO_{4+\delta}$ itself.

Already it is known that the electronic transport in $La_2CuO_{4+\delta}$ couples strongly to its magnetism. When a sufficiently strong magnetic field is applied perpendicular to the CuO_2 planes, a metamagnetic transition[8] occurs below T_N due to field-induced reorientation of the Cu^{2+} spins. At this transition there is a substantial *decrease* in the electric resistivity, indicating that Cu^{2+} spins and transport carriers are strongly correlated. Given the quasi-2D character of the crystal structure, large electronic anisotropy may be expected. However, the extent of zero-field transport anisotropy is controversial and seems to depend sensitively on impurity content in $La_2CuO_{4+\delta}$. Crystals grown from a PbO-containing flux show a huge resistivity anisotropy;[9] whereas, those grown in either a Li_2O-B_2O or CuO-based flux[10] have a resistivity perpendicular to the CuO_2 planes ($\rho_\perp$) no more than 20 times the resistivity parallel to the planes ($\rho_\parallel$). More recent measurements[11] on crystals grown from purely CuO flux show an anisotropy $\rho_\perp/\rho_\parallel$ that varies from 20 to 100.

In an attempt to understand more completely the underlying physics in $La_2CuO_{4+\delta}$, we have measured the temperature dependence and anisotropy of the electrical resistivity and thermoelectric power S as a function of small hole doping δ. Crystals as large as $3\times3\times0.3$ cm^3 were grown from CuO-rich La_2O_3-CuO melts in platinum crucibles, the size of which determined the maximum crystal size. After being quenched from high temperature, crystals were removed from the flux and annealed in an appropriate atmosphere. Depending on the environment chosen, the Néel temperature T_N, and consequently the hole doping, could be "tuned" from about 255 K to as high as 328 K, without broadening the magnetic transition [full width at half maximum (FWHM) of the susceptibility peak being less than 15 K in all cases]. Attempts to raise T_N further led to dissociation of the samples; therefore, we associate the highest T_N with $\delta = 0$. The very sharp magnetic transitions produced by the annealing process indicate a homogeneous distribution of oxygen in the sample bulk.

The anisotropic electrical resistivity was determined using both Montgomery[12] and standard four-probe configurations on crystals polished to have well-defined geometries. Agreement between the two resistivity techniques was checked on several crystals with differing geometries and found to be quite good. The absolute thermoelectric power was determined relative to copper. The standard technique employed used a maximum relative temperature gradient ($\Delta T/T$) of $\sim 0.5\%$. Tests against constantan and platinum gave thermoelectric powers within 5% of their accepted values.

Figure 1 shows the resistivity parallel $\rho_\parallel$ and perpendicular $\rho_\perp$ to the CuO_2-plane direction of a $La_2CuO_{4+\delta}$ crystal annealed in air. From approximately 300 to 100 K, $\rho_\parallel$ is only weakly temperature dependent and of magnitude 0.1 Ω cm, a value well outside the metallic conduction limit. Below ~ 100 K, $\rho_\parallel$ fairly abruptly takes on a semiconductorlike behavior before it is interrupted by the appearance of surface superconductivity below $T_c \simeq 40$ K. It is not clear what causes the upturn in $\rho_\parallel$ but it appears as a feature common to all crystals in which the resistivity can be measured to sufficiently low temperatures. A pos-

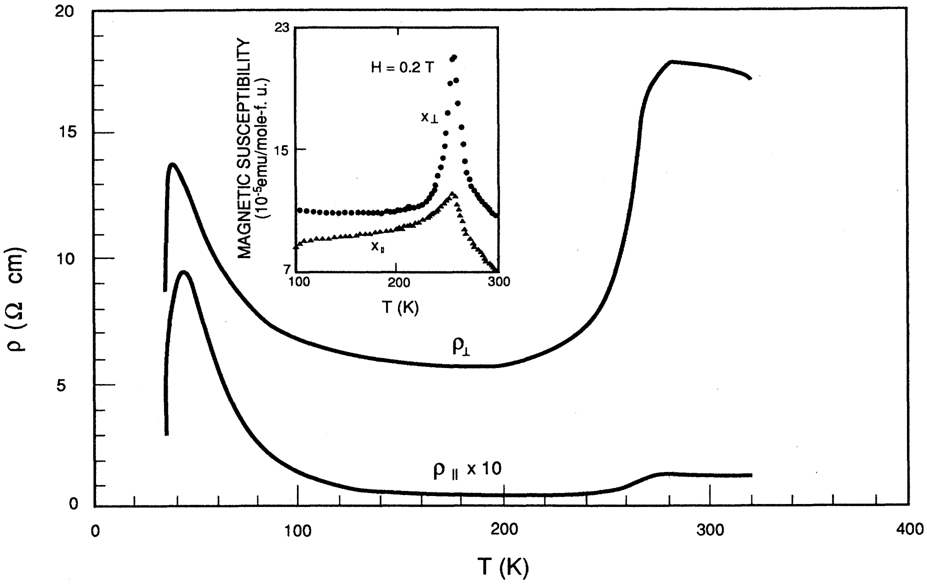

FIG. 1. Temperature dependence of the in-plane ($\rho_{\parallel}$) and out-of-plane ($\rho_{\perp}$) resistivity determined by the Montgomery method on an air-annealed La_2CuO_4 crystal. The inset shows the temperature-dependent magnetic susceptibility of a similarly prepared crystal for a 2-kG field applied parallel ($\chi_{\parallel}$) and perpendicular ($\chi_{\perp}$) to the CuO_2-plane direction.

sible interpretation is a change from diffusive transport at high temperatures through nearest-neighbor hopping at intermediate temperatures to variable range hopping below 100 K, as suggested from studies on La_2CuO_4 crystals grown from PbO flux.[9] The weak anomaly in $\rho_{\parallel}$ near 255 K is associated with antiferromagnetic order. The inset of Fig. 1 shows a sharp peak in the magnetic susceptibility at 257 ± 0.5 K for a crystal prepared under similar conditions. (For convenience we identify the Néel temperature T_N as the temperature where χ is maximum, although this definition could lead to an overestimate of T_N by ~ 4 K.[8]) A much more pronounced effect on the resistivity at T_N is evident in the resistivity perpendicular to the CuO_2 planes. The rather enormous decrease in $\rho_{\perp}$, ~ 10 Ω cm, at T_N is much larger than would be expected simply from the removal of spin-disorder scattering.[13] Removing a surface layer of the crystal reduces the diamagnetic response below T_c but the resistivity anomaly at T_N remains. The data in Fig. 1 also show a substantial anisotropy in ρ, with $\rho_{\perp}/\rho_{\parallel} \sim 150$ at room temperature.

After these measurements, the crystal was annealed in nitrogen. As shown in Fig. 2, nitrogen annealing produces a modest increase in the magnitude of $\rho_{\parallel}$ and $\rho_{\perp}$ and changes the temperature dependence of both; although, there is still an abrupt upturn in the resistivities at ~ 100 K. Magnetic-susceptibility measurements on this nitrogen-annealed crystal show a sharp peak at ~ 295 K, indicating an increase in T_N and a decrease in δ relative to the air-annealed conditions. Only a very weak anomaly in the resistivity could be detected in the vicinity of T_N. There remains, however, substantial anisotropy in the resistivity which decreases slowly with decreasing temperature. We have tried to fit the temperature dependence of $\rho_{\parallel}$ to $\ln\rho_{\parallel} \propto (1/T)^{\alpha}$, where α is a constant, but failed to find fits reliable over an extended temperature interval, contrary to previous reports[9-11] on less well-characterized samples.

Further anneals of this crystal in vacuum enhance T_N to ~ 328 K and increase $\rho_{\parallel}$ (300 K) to ~ 350 Ω cm. Because of the extremely large resistivity in this case, it was not possible to make reliable temperature-dependent studies. The magnitude of ρ, however, does suggest that in this case we are at or at least very near the limit of halfband filling, i.e., $\delta = 0$.

The thermopower of an air-annealed crystal is shown in Fig. 3. The thermopower in the CuO_2 planes, $S_{\parallel}$, is essentially temperature independent above ~ 260 K, but drops precipitously by ~ 60 μV/K to another plateau below 230 K before beginning a rather sharp decrease near 100 K, which is where ρ increases abruptly. Near 40 K, $S_{\parallel}$ falls

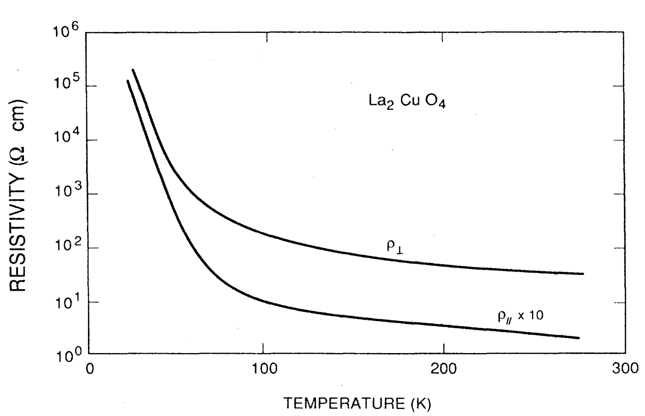

FIG. 2. Temperature dependence of the in-plane ($\rho_{\parallel}$) and out-of-plane ($\rho_{\perp}$) resistivity of the crystal used in Fig. 1 after annealing in nitrogen. The anisotropic resistivity was determined by the Montgomery method.

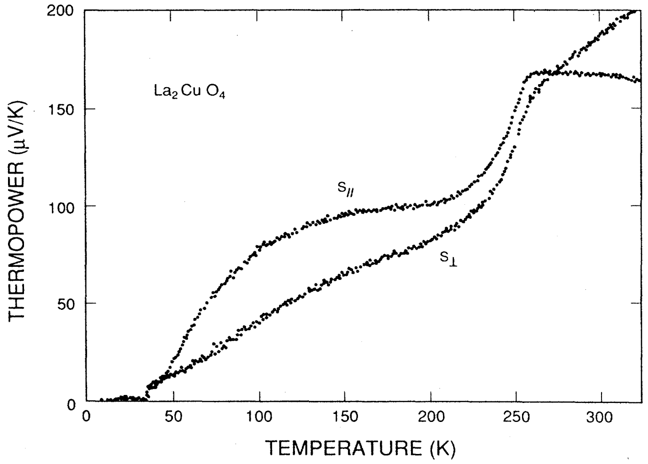

FIG. 3. In-plane ($S_{\parallel}$) and out-of-plane ($S_{\perp}$) thermoelectric power of an air-annealed La_2CuO_4 crystal as a function of temperature.

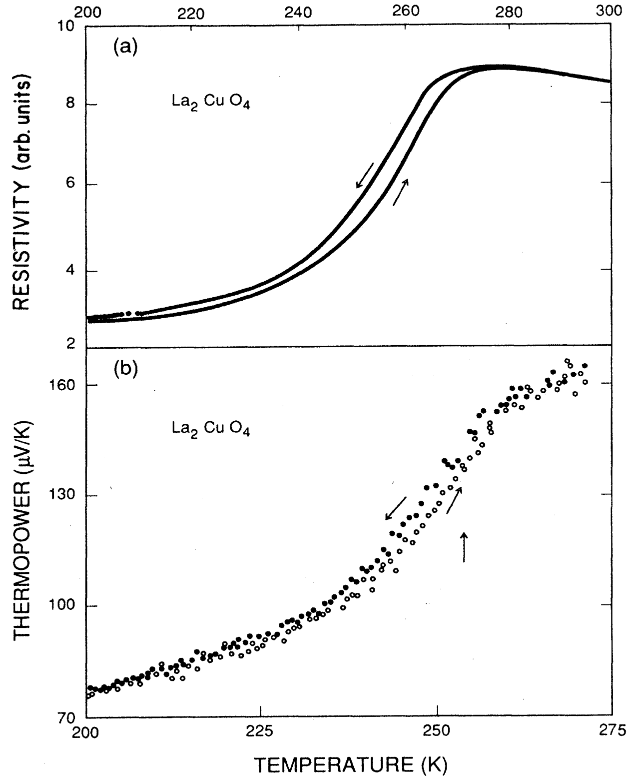

FIG. 4. (a) Out-of-plane resistivity ($\rho_{\perp}$) of an air-annealed crystal of La_2CuO_4 measured on cooling and warming through the Néel temperature T_N. (b) Out-of-plane thermopower ($S_{\perp}$) obtained on cooling and warming through T_N. The vertical arrow marks the temperature where a peak in the susceptibility of this crystal appears.

to zero because of surface superconductivity. On the other hand, $S_{\perp}$ increases approximately linearly with temperature above 40 K except for anomalous behavior around 255 K. The dramatic changes in both $S_{\parallel}$ and $S_{\perp}$ again are associated with antiferromagnetic order since magnetic-susceptibility measurements on this crystal show a sharp peak at 255 ± 0.5 K. It is interesting that, except for the behavior near 255 K, the temperature dependences of $S_{\parallel}$ and $S_{\perp}$ are similar to those observed[14] in metallic-like $YBa_2Cu_3O_7$. However, the magnitudes of S in these two cases are quite different.

Figure 4 shows an expanded view of $\rho_{\perp}$ and $S_{\perp}$ for air-annealed crystals at temperatures near T_N. Clear hysteresis upon warming and cooling are found in both measurements. The hysteresis in $\rho_{\perp}$($\sim$5 K) is somewhat more pronounced because in the thermopower measurement a temperature gradient of $\sim$1 K was used in this temperature range. These experiments were done very carefully on several different crystals, always in good thermal equilibrium, and always the hysteresis was reproducible. This hysteresis does not appear to be a magnetic effect since the maximum thermal hysteresis (<0.5 K) in magnetic-susceptibility measurements is much less than hysteresis in the transport properties. Thus, the Néel transition appears to be second order, as expected; whereas, the transport shows definite thermal history dependence.

There are several issues raised by these results. The first concerns the variation in transport properties produced by different anneals, i.e., oxygen content. Although significant variations are found in ρ and S, the Hall coefficient R_H remains positive, independent of the annealing environment. Relative to air or oxygen anneals, inert gas and vacuum anneals increase the magnitude of both the resistivity and T_N. In the last case (vacuum anneal), the electronic specific heat is <0.2 mJ/mole K^2. Finally, though not measured on these crystals, Johnston *et al.*[2] have reported that the tetragonal-to-orthorhombic transition temperature increases and magnetic defects are reduced upon oxygen removal. These observations together indicate that the oxygen stoichiometry is always equal to or greater than that required for halfband filling, giving a Mott-Hubbard antiferromagnetic, insulating ground state, that any attempt to reduce the oxygen content to give less than half filling induces dissociation of the sample and that very small variations in the number of carriers change dramatically the transport and magnetic properties of $La_2CuO_{4+\delta}$.

The next issue to be addressed is the appropriateness of a band picture to $La_2CuO_{4+\delta}$. Hall effect measurements on an air-annealed crystal give a temperature dependence of R_H similar to that of $\rho_{\parallel}$. The Hall coefficient at room temperature for transport in the CuO_2 planes is 1.1×10^{-9} Ω cm/G. An estimate of the Hall mobility μ_H from $\rho_{\parallel}$ and R_H at room temperature gives $\mu_H \sim 0.9$ cm^2/V s, a value much too small to be associated with bandlike conduction. Further, within the free-electron approximation, the electronic mean free path, estimated to be $\sim$1 Å, is extremely short, which suggests that the concept of extended band states is not applicable to La_2CuO_4. Thus, the Boltzmann equation cannot be used to calculated transport properties.

Perhaps the most significant issue is the unexpected, enormous transport anomalies found at T_N in air-annealed crystals. Differential scanning calorimetry on an air-annealed crystal of $La_2CuO_{4+\delta}$ shows no evidence for a specific-heat anomaly at T_N within the experimental resolution of $0.1R\ln 2$. This result implies that most of the entropy associated with divalent copper spins has been removed through 2D short-range ordering at temperatures $T > T_N$. Thus, reducing spin scattering[13] or removing spin entropy[15] at T_N cannot explain the transport anomalies. Further, because ρ and S decrease abruptly at T_N, opening a gap on the Fermi surface,[16] as in Cr, is not an appropriate interpretation for the anomalies either. One natural inference from the observed behavior, combined with the appearance of a large magnetoresistance[8] when the metamagnetic-phase boundary is crossed, is that there is an extraordinary interrelationship between 3D spin ordering and transport by itinerant holes. Such behavior may be relevant to superconductivity in La_2CuO_4-based systems. However, without a specific microscopic theory for this interrelationship, further interpretation of our results is not possible.

Another possible explanation for the transport anomalies at T_N involves the formation and/or destruction of twin structures induced through magnetic stress. In orthorhombic $YBa_2Cu_3O_7$, very fine twin structure with spacings of ~250 Å are produced by thermal cycling below approximately 230 K.[17] Warming the sample to room temperature coarsens the twins. Although we are not aware of similar observations on orthorhombic $La_2CuO_{4+\delta}$, we might expect similar behavior. Preliminary thermal expansion experiments[18] on $La_2CuO_{4+\delta}$ show an increase in the thermal expansion coefficient in the CuO_2 planes as the temperature is reduced through T_N and hysteresis upon cycling through T_N. Thus, a possible interpretation for the appearance of transport anomalies is that magnetoelastic stress, associated with Néel ordering, induces the abrupt formation of a refined twin structure. The reduced spatial coherence[17] of the crystallographic structure could, in turn, move the electronic state away from the Mott-Hubbard insulator limit. Hysteresis in both the resistivity and thermopower can be understood as arising from metastability of the coherent twin boundaries produced by thermal cycling. One might imagine that a relatively fine twin structure exists in nitrogen-annealed samples already at temperatures above T_N because of the more strongly orthorhombically distorted structure in these crystals. Consequently, reduced transport anomalies at T_N might be expected. Though conceivable, these suggestions do not clearly explain why such dramatic transport anomalies are found at T_N in air-annealed crystals but not in those annealed in nitrogen.

In summary, we have found striking anomalies in the transport properties of weakly hole-doped $La_2CuO_{4+\delta}$ crystals at their Néel temperature, suggesting a strong coupling between magnetic order and transport. Although possible explanations for these behaviors are given, clearly much more work is required to understand them completely.

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