Isotropic negative magnetoresistance in $La_{2-x}Sr_xCuO_{4+y}$

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Measurements are reported of the magnetoresistance of thoroughly characterized single crystals of $La_{2-x}Sr_xCuO_{4+y}$ with $0.02 \leq x \leq 0.1$. Above the superconducting critical temperature, the conductance of the CuO_2 layers increases logarithmically with temperature at low T. However, the magnetoresistance is isotropic and negative, inconsistent with coherent backscattering or conventional interaction effects, suggesting that spin scattering limits the conductance.

The lamellar copper oxides can be viewed as antiferromagnetic semiconductors which are superconducting when degenerately doped. The semiconducting state is the result of strong correlations—correlations that are thought to be important in causing the superconductivity as well. We recently reported[1-3] detailed studies of the transport properties of single crystals of La_2CuO_4 in which the charge-carrier (hole) density was varied by changing the oxygen concentration. We showed, from measurements of the dc and ac conductivity, the dielectric constant, and the Hall effect that the behavior of doped La_2CuO_4 is closely analogous to that of conventional doped semiconductors, like P-doped Si, approaching the insulator-to-metal transition. The oxygen acts as an acceptor with a small binding energy, ~ 35 meV, for the excess hole, and the hole mass is $\sim 2m_e$. The hole is bound in an orbit with an in-plane radius of about 8 Å, and when the density is high enough that neighboring orbits begin to overlap, the localization length grows rapidly with the acceptor density. However, whereas in three-dimensional (3D) semiconductors this leads to the insulator-to-metal transition, there can be no true transition in La_2CuO_4 because the growth in the localization length is two dimensional.[2,3] Instead, one expects a crossover from strong to weak localization occurring at a progressively lower temperature as the concentration of acceptors is increased.

To test this idea we examined the conductance of a number of single crystals of $La_{2-x}Sr_xCuO_{4+y}$. Initial results seemed to indicate[4] that this system behaved like a conventional 2D disordered metal for $x \gtrsim 0.01$: For such concentrations, the conductance per square per CuO_2 layer is $\gtrsim e^2/h$, and, at low T, the conductance increases logarithmically with temperature with a coefficient that is also $\sim e^2/h$. In conventional disordered metals, corrections to the conductance can arise from coherent backscattering (weak localization)[5] or from electron-electron interactions[6] and both mechanisms give logarithmic corrections in 2D because they involve quantum-mechanical diffusion.

To identify the origin of the logarithmic conductance, we have carried out magnetoresistance measurements. In conventional disordered 2D metals, such measurements discriminate between coherent backscattering and electron-electron interactions. We have found that the magnetoresistance of $La_{2-x}Sr_xCuO_{4+y}$ cannot be explained by either of these mechanisms. Instead, the magnetoresistance is similar to that found in Kondo systems and spin glasses, in which the conductance is limited by spin scattering.

Crystals were grown using CuO flux methods at Massachusetts Institute of Technology (MIT) and Nippon Telephone and Telegraph Corporation (NTT); the growth techniques are described elsewhere.[7,8] The large crystals produced by these methods often contain cracks and flux inclusions, so small ($\sim 1\times1\times3$ mm^3), flawless parallelepipeds were cut from the large boules. The resistance was then measured by both the Montgomery and conventional four-probe measurements. These techniques and those used for the Hall effect measurements are described in Ref. 1. The magnetoresistance measurements were made in conventional and split-coil Bitter magnets.

We emphasize that the homogeneity of our crystals has been examined with thoroughness. Using crystals prepared in an identical manner and, where possible, a piece of the identical crystal, we have studied three phase transitions. The tetragonal-to-orthorhombic transition was examined by neutron[9] and x-ray[10] scattering, the transition to antiferromagnetic long-range order (Néel) by neutron, magnetic susceptibility,[1] and μSR techniques,[11] and the superconducting transition by magnetic moment, resistance, and μSR measurements. Because these transitions have critical temperatures that vary rapidly with chemical composition, inhomogeneities broaden them. Using the tetragonal-to-orthorhombic transition, we have shown that the total Sr and oxygen heterogeneity in crystals with the maximum superconducting T_c is less than ± 0.01 of the Cu atom density. For crystals containing no Sr and oxygen excess less than $y \sim 0.01$, the sharp Néel transition shows that the oxygen content is homogeneous to $\Delta y \sim 0.001$. Furthermore, the observation[12] that phase separation occurs at concentrations $y > 0.03$ indicates that oxygen diffuses rapidly. Since we see no evidence of this phase separation for $y \lesssim 0.01$, the oxygen must be uniformly dispersed. Our crystals appear, therefore, to be quite homogeneous; it appears that other workers have been less successful in preparing homogeneous ceramics.[13]

Despite this chemical homogeneity in the bulk, some crystals were found to have highly conducting regions near the surface. We suspect that this was sometimes the result of a very thin surface layer containing excess oxygen or Sr. However, it was also possible to induce such a conducting region by exposure to an aqueous solution of HCl, suggesting that the surface can also be made conducting by modifying surface states in such a way that there is an accumulation of holes near the surface. We found, in most cases, that polishing to remove surface nonstoichiometry and etching in 1% Br in methanol produced quite reproducible results. In addition, contacts made with silver paint to Br-etched surfaces had comparatively low resistance.

We have measured the anisotropic conductivity, the Hall effect, and the magnetoresistance of three $La_{2-x}Sr_xCuO_{4+y}$ crystals with $x = 0.02$ (sample No. 1), $x = 0.06$ (sample No. 2), and $x = 0.1$ (sample No. 3). Sample No. 1 is actually a small piece of a large crystal that was studied extensively by neutron scattering.[14] It shows short-range two-dimensional spin correlations with no 3D Bragg scattering. The correlations fluctuate rapidly at high T but slow down at low T, indicative of a spin-glass state. This crystal shows no evidence of superconductivity, but sample No. 3, on the other hand, with $x = 0.1$, has zero resistance below 9 K. The conductivity is highly anisotropic for all the crystals, typically 200–500 near room temperature.

Our measurements of the Hall coefficient R_H as a function of T for the crystal with $x = 0.1$ is consistent, in detail, with the results of Suzuki[15] for thin films. Using R_H to determine the carrier density, we had found[1] a mobility $\mu = 3-4$ cm^2 V s, independent of oxygen content, for La_2CuO_{4+y}. In the same way we find $\mu \sim 7$ cm^2/V s for sample No. 1 and $\mu \sim 10$ cm^2/V s for sample No. 3. The carrier density determined from R_H agrees well with that inferred from the chemical composition as determined from the tetragonal-to-orthorhombic transition temperature and the lattice constants.

As mentioned earlier, the behavior of La_2CuO_{4+y} is closely analogous to that displayed by doped semiconductors. The activated temperature dependences[1] of the Hall effect and the conductivity at low doping densities result from thermal ionization of the shallow impurities. As the doping level increases, the activated dependence gives way to more weakly temperature-dependent conductivity. In doped semiconductors this is the hallmark of the impurity-band insulator-to-metal transition.

However, as illustrated in Fig. 1 for sample No. 1, in samples of $La_{2-x}Sr_xCuO_{4+y}$ which are at densities high enough that metallic behavior would be observed in a

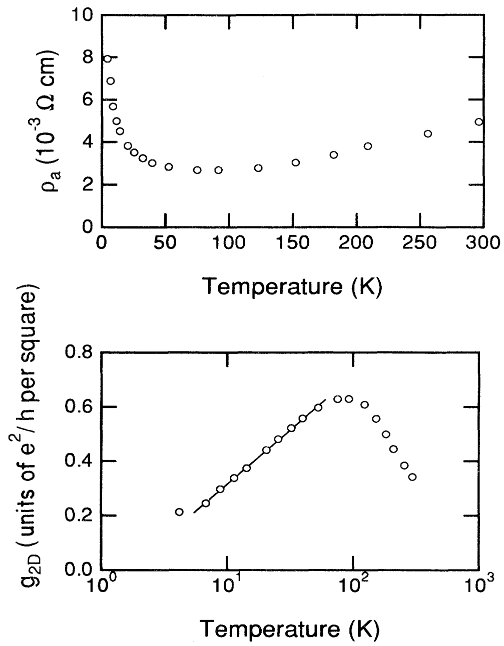

Fig. 1. (a) In -plane resistivity ρ_a vs T for sample No. 1. (b) Same data plotted as conductance per square per CuO_2 layer, g_{2D}, vs $\log_{10}T$.

doped semiconductor, that is, when the impurity orbits begin to overlap, the resistivity exhibits new, characteristic behavior. First, at high temperatures one sees the same increase of the resistivity linear in T observed in the normal state of the highest T_c superconductors. This shows that the quality of sample No. 1 is unusually high. Normalizing to the inverse of the carrier density, the slope is comparable to that found in single crystals of $YBa_2Cu_3O_7$: The Hall effect gives a hole density close to the Sr concentration, $x = 0.02$. With this density and using $m^* = 2m_e$ for the effective mass of the holes,[2,3] we find a scattering time $\sim 3\ \hbar/kT$, comparable to that[16] in $YBa_2Cu_3O_7$. The extrapolation of this linear dependence to $T = 0$ gives $k_F l \sim 2$.

Second, as seen in the lower panel of Fig. 1, at low T the conductance is proportional to $\log_{10}T$ over more than a decade of temperature. The deviation from the logarithmic dependence at the lowest temperatures may result from residual surface conductivity. The proportionality to $\log_{10}T$ is typical of conventional 2D disordered metals,[5] but in those the log term is usually a small correction to the total conductance, whereas it dominates the conductance in $La_{1.98}Sr_{0.02}CuO_{4+y}$ for $T < 80$ K. From a different viewpoint, however, the $\log_{10}T$ term does not seem exceptionally large, since, as predicted by the theories of weak localization[5] and interaction,[6] we find[4] that the coefficient of the $\ln T$ conductance is $\sim e^2/h$ whenever the conductance is $\gtrsim e^2/h$.

The *magnetoresistance* of our crystals is, however, very different from that of conventional 2D disordered metals. Figure 2 shows the fractional change in resistance for

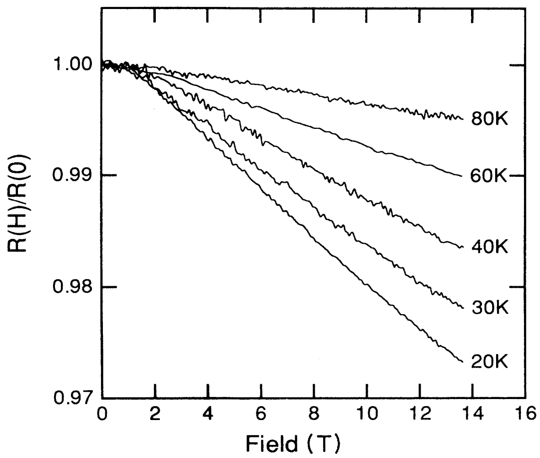

Fig. 2. Magnetic field dependence for sample No. 1 at various temperatures and for **H**||**b**. The dependence is the same for **H**||**a**.

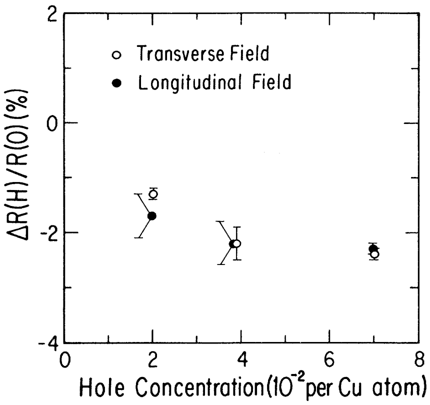

Fig. 3. Fractional magnetoresistance vs hole concentration, determined by Hall measurements, for transverse and longitudinal fields. Measurements were made at 35 K and 8 T.

sample No. 1 with **H**||**b** and **E**||**a** for temperatures between 20 and 80 K. In the orthorhombic notation used throughout (space group *Cmca*), **a** is parallel to the CuO_2 layers and is indistinguishable from **c** because of twinning. For convenience we use **a** to denote an arbitrary in-plane direction. The magnetoresistance is much larger than that usually found in 2D metals at such high temperatures.[5]

A much more surprising feature of the magnetoresistance emerges from measurements of its anisotropy. Specifically, we find that the magnetoresistance is independent of the direction of the magnetic field. This is illustrated in Fig. 3 where we plot the fractional in-plane magnetoresistance $\Delta R/R$ at $H=8$ T and $T=35$ K for several crystals with different x and for both **H**||**b** and **H**||**a**. We also checked that $\Delta R/R$ is the same for **H**||**E** and **H**⊥**E** when both **H** and **E** lie in the CuO_2 layer. The relatively high temperature of 35 K was chosen for the comparison between samples because the crystals with $x \geq 0.06$ show very large *positive* magnetoresistance at lower T, indicative of incipient superconductivity. As the temperature is lowered, this highly anisotropic magnetoresistance makes it impossible to measure the isotropic negative magnetoresistance accurately.

We note that Fiory *et al.* reported[17] negative magnetoresistance in nonsuperconducting crystals of Bi-Sr-Cu-O which, like our crystals, show a logarithmic temperature dependence of the conductance. They reported anisotropies of order 2–3 and ascribed the effect to weak localization.

The isotropy of the magnetoresistance measured at 35 K indicates that it results from a spin, rather than orbital, effect. This excludes as possible mechanisms coherent backscattering and some of the electron-electron interaction effects. Isotropic magnetoresistance is predicted for the particle-hole scattering contribution to the electron-electron interaction,[5,6] but such magnetoresistance is expected to be positive rather than negative. For the electron-electron interaction mechanism, the scattering is appreciable only when the Zeeman-split levels are separated by less than kT. The effect thus depends only on $g\mu_B SH/kT$. In Fig. 4 we show that our results do, in fact, scale reasonably well when plotted against H/T.

Several surprising features emerge from Fig. 4. First, spin effects like the particle-hole channel described above, are expected to be quadratic in H/T until the Zeeman energy is comparable to kT, which happens when $H/T \sim 1T/K$ for $g=2$ and $S=\frac{1}{2}$. We find, instead, clear deviations from quadratic behavior for $H/T \gtrsim 0.1$. Second, the dependence is, in fact, quite linear in H/T. Last, the scaling persists up to 80 K where the $\log_{10}T$ component is a small fraction of the total conductance. This means that the magnetic field does not solely affect the $\log_{10}T$ correction to the conductance as it does for coherent backscattering and interaction effects.

Isotropic negative magnetoresistance has been seen[18] in a variety of metals containing fluctuating spins: Kondo systems and spin glasses. The authors have ascribed this

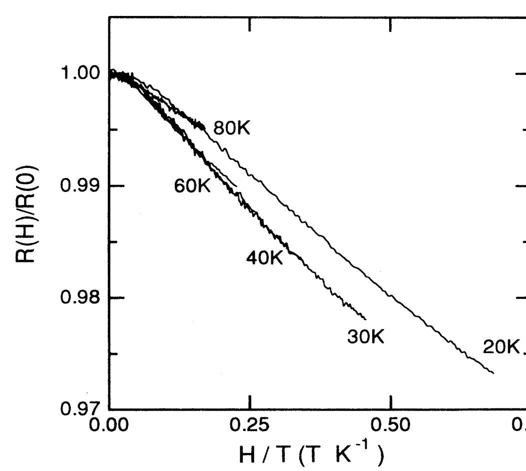

Fig. 4. Data of Fig. 3 plotted vs. H/T.

to a reduction of spin scattering by the magnetic field. We suppose that a similar mechanism is at work in $La_{2-x}Sr_xCuO_{4+y}$. The low mobility (~ 3) with the mass of $\sim 2m_e$ requires a scattering time of 10^{-14} s, comparable to $\hbar/J$, suggesting that the charge carriers are strongly scattered by the fluctuating Cu spin system.

Neutron-scattering measurements[19] have recently revealed that the imaginary part of the spin susceptibility $\chi''(q,\omega)$ when integrated over q scales with ω/T. Such a form of χ'', a homogeneous function of ω/T, is sufficient to give a resistance linear in T if the conductance is limited by spin scattering. Furthermore, one expects an applied magnetic field to introduce a gap in the spin-excitation spectrum, and it is likely that the scaling of χ'' with ω/T leads to the scaling of magnetoresistance with H/T.

The detailed dependence of resistance on H/T depends on how an external field changes χ''. However, we note that the quadratic dependence on R on H/T for $g\mu_B SH < kT$ is expected for a single free spin. For a sample like sample No. 1, with antiferromagnetic correlations that extend over ~ 100 spins, one expects the energy scale to be reduced by a factor ~ 10 leading to deviations from quadratic behavior about $g\mu_B SH/kT \sim 0.1$ as observed.[20]

In conclusion, whereas some of the qualitative features of the transport in $La_{2-x}Sr_xCuO_{4+y}$ with $x \geq 0.02$ are similar to those in conventional 2D metals, the magnetoresistance exhibits qualitatively different behavior. The $\log_{10}T$ conductance appears, at first sight, to be the result of coherent backscattering or electron-electron interactions. However, the isotropic negative magnetoresistance suggests strong coupling between the fluctuating Cu spins and the charge carriers. It is nonetheless clear that the deviations from metallic behavior for sample No. 1, with only 2% holes, are no larger than expected for a disordered two-dimensional metal. The insulator-to-metal transition is thus very close to the antiferromagnetic phase boundary rather than near the superconducting phase boundary (at $\sim 5\%$) as previously believed. A similar conclusion was arrived at by Chen *et al.*[2,3] from measurements of the dielectric constant in the antiferromagnetic insulating regime with $\leq 1\%$ holes. Finally, we emphasize that the transport properties evolve continuously with hole concentration, and so an understanding of some unusual features, such as the isotropic negative magnetoresistance, which can be examined more thoroughly in the lightly doped regime, may help elucidate the origin of the superconductivity.

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