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# Conductivity and Hall coefficient in $La_2CuO_{4+y}$ near the insulator-metal transition

N. W. Preyer,* R. J. Birgeneau,* C. Y. Chen,* D. R. Gabbe, H. P. Jenssen,
M. A. Kastner,* P. J. Picone,† and Tineke Thio*
*Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

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Measurements are reported of the conductivity, its anisotropy, and the in-plane Hall coefficient for a single crystal of $La_2CuO_{4+y}$ with $y$ varied from 0%–1.5%. The conductivity is thermally activated with a single activation energy at high temperatures and with a continuously decreasing activation energy below ∼50 K. The anisotropy is as large as 500 at high temperatures, falls sharply to 10–20 at ∼50 K, and then is only weakly $T$ dependent at lower temperatures. The Hall coefficient is simply activated above ∼50 K (with an activation energy similar to that of the in-plane conductivity), and has a peak at lower temperatures. All these features are evidence for a change in the transport mechanism near 50 K. The low-temperature conductivity is consistent with thermally assisted tunneling between localized states at the Fermi energy. The high-temperature process arises from thermal activation of carriers into a band of highly anisotropic states. The low mobility associated with these states makes it impossible, however, to determine whether they arise from impurities or are states near a band or mobility edge.

## I. INTRODUCTION

Since the discovery[1] of high-temperature superconductivity in $La_{2-x}Ba_xCuO_4$ and other copper oxides, it has become clear that the lamellar $CuO_2$ superconductors have a common global phase diagram.[2,3] At low hole density the system is an antiferromagnetic insulator, but a concentration of a few percent holes is enough to destroy the Néel state and create a spin-glass phase.[2] The addition of holes also causes the insulator-metal transition (IMT). Because the IMT is found so close to the superconducting region, it is important to understand this transition in detail.

In this paper we report the results of a study of the transport in single crystals of $La_2CuO_4$ approaching the IMT, with hole concentration altered by annealing the crystals in various chemical potentials of $O_2$. We find evidence, both from the conductivity tensor and the Hall coefficient, of a change in the carrier transport mechanism near 50 K. Below this temperature, holes move by hopping between localized states at the Fermi energy, whereas at higher temperatures holes move by thermal activation into highly anisotropic states. Because of the very low mobilities, however, we are unable to determine whether these states are near a band or a mobility edge.

## II. EXPERIMENTAL DETAILS

Single crystals of $La_2CuO_4$ were grown by the top-seeded solution method in a CuO flux. A Laue camera was used to determine the sample orientation: the $a$-$c$ plane (orthorhombic notation) grows parallel to the surface of the melt and the dimension along the $b$ direction is typically the smallest. Details of the crystal growth technique have been published elsewhere.[4]

The Montgomery[5] method is commonly used to determine the conductivity tensor of small uniaxial crystals of insufficient size for conventional four-probe measurements. The Montgomery method can be used with either point or line contacts; line contacts are preferred for their strength and lower contact resistance. All measurements reported here were therefore made with line contacts, although some results were repeated with point contacts. The four leads were placed along the edges of the crystal, parallel to one of the in-plane tetragonal axes. This geometry did not allow the measurement of the in-plane anisotropy. Any in-plane anisotropy is expected to be small because of the twinning of orthorhombic domains, and because the orthorhombic distortion of the tetragonal structure is so slight. To verify this, the in-plane anisotropy was also measured by the Montgomery method, with a different lead geometry, and was found to be just 1.4. All contacts were made with silver paint. These had relatively high resistance (∼100 Ω at 300 K, several MΩ at 4.2 K) and limited the range of sample resistances which could be measured.

Most of the crystals were grown in air. Earlier conventional four-probe measurements of resistivity[6] on some of these showed nearly isotropic hopping conductivity, a result which we have confirmed with the Montgomery method for those samples. However, there is apparently a large variation in behavior from sample to sample. Some of the crystals grown in air had anisotropic conductivity, and one, grown in an oxygen ambient, appeared closest to ideal. It displayed the largest anisotropy and reached the highest Néel temperature when reduced. This crystal was about 3 cm square ($a$-$c$ plane) and 1 mm thick ($b$ axis) as grown, and the piece cut for transport measurements was $6.4\times2.6\times0.9$ mm$^3$. Most of the results discussed here are for the latter crystal, although qualitatively similar behavior was observed for a crystal grown in air.

The Hall effect was measured in both four- and five-probe configurations with identical results. The Hall voltage was measured by a lock-in technique at 28 or 37 Hz with sufficiently small currents to prevent sample heating.

TABLE I. Summary of sample processing and measurements. $T_N$ is the Néel temperature determined from the peak of the susceptibility. The processing sequence and conditions are given by step (with the as-grown crystal given No. 1), gas, $T$, and time. All oxidation steps were oven quenched. Steps 3 and 4 gave $T_N$ essentially identical with the as-grown sample. $E_a$, $E_b$, and $E_H$ are the activation energies of the in-plane conductivity, out-of-plane conductivity, and Hall coefficient, respectively. $T_N$ was used to estimate the mole% excess oxygen, while the Hall coefficient gave estimates for the hole concentration $p$.

| $T_N$ (K) | Step | Gas | $T$ (°C) | Time (h) | $E_a$ (meV) | $E_b$ (meV) | $E_H$ (meV) | Excess O[a] (mole%) | $p(T=300$ K) (% holes) | $p(T=\infty)$ (% holes) |
|---|---|---|---|---|---|---|---|---|---|---|
| 320 | 8[b] | Ar | 725 | 2.5 | | | | | | |
| 310 | 2 | Ar | 665 | 2 | 41.5(3) | 27.1(7) | 34(1) | 0.5(3) | 0.08(1) | 0.21(4) |
| 285 | 6 | Ar | 510 | 6 | 28.6(6) | 12.9(3) | 22(1) | 1.0(3) | 0.15(1) | 0.38(3) |
| 260 | 5 | Ar | 400 | 8 | 23.1(3) | 9.5(1) | 24(1) | 1.3(3) | 0.30(2) | 1.74(6) |
| 240 | 1[c] | $O_2$ | ··· | ··· | 24(1) | 8.2(2) | 18(2) | 1.4(3) | 0.5(1) | 0.9(3) |
| | 3 | $O_2$ | 385 | 13 | | | | | | |
| | 4 | Ar | 330 | 20 | | | | | | |
| 215 | 7[d] | $O_2$ | 600 | 6 | | | | | | |

[a] Reference 9.

[b] Sample broke after annealing.

[c] As grown.

[d] Trace superconductivity ( < 0.01% Meissner effect) at 30 K.

The sample was placed in an oscillating magnetic field (0 to 6 kG) with a period of about 20 s. The resulting slow modulation of the lock-in-amplifier output was recorded and averaged with a digital oscilloscope. To remove the effects of magnetoresistance the difference of positive and negative magnetic field data was taken to measure the Hall voltage. Because of the sample geometry, measurements could only be made with the field perpendicular to the $CuO_2$ planes.

The oxygen content of the crystal was changed by annealing it in a furnace in an atmosphere of dried oxygen or argon for various times and temperatures. Since there was undoubtedly some diffusion of air into the furnace during argon annealing, there was a small partial pressure of oxygen present. Thus the variation of ambient and temperature corresponds to a variation of the oxygen chemical potential. The samples were etched for 90 s in 1% HCl after each step to remove any enriched or depleted surface layers. A superconducting quantum interference device (SQUID) magnetometer was used to measure the magnetic susceptibility, which characterizes the oxygen content and homogeneity, after each processing step. All measurements were made in a 5-kG magnetic field applied along the $b$ axis. The resulting states are listed in Table I in order of decreasing Néel temperature, determined as discussed below.

## III. RESULTS

In Fig. 1 we plot the magnetic susceptibility as a function of temperature after three stages of oxidation or reduction of the sample. The pronounced peak in the susceptibility results[7] from a bilinear coupling between the uniform and staggered moments arising from Dzyaloshinsky-Moriya antisymmetric exchange made allowed by the staggered rotation of the CuO octahedra in the orthorhombic phase. As shown by Thio *et al.*,[7] the peak occurs at the Néel temperature. The crystal had $T_N = 240$ K as grown, and $T_N$ varied from 320 to 215 K as the oxygen concentration was changed. After one or two of the preparation stages, such as that with $T_N = 215$ K (Fig. 1), two peaks appeared in the susceptibility; this is clear evidence of heterogeneity. The latter preparation showed superconductivity with $T_c \sim 30$ K, but the small Meissner fraction, $\sim 0.01\%$, and the coexistence of superconductivity and antiferromagnetism, are strong evidence that this state is heterogeneous. Recently, structural evidence for heterogeneity in oxygen-doped superconducting $La_2CuO_4$ has been reported.[8] However, for lower oxygen content this does not appear to be the case. Preparations that show clear evidence of heterogeneity will not be discussed further. The susceptibility peak is quite sharp for the highest $T_N$, indicating that the oxygen content is very homogeneous. That short annealing periods produce very homogeneous samples is evidence that the oxygen dif-

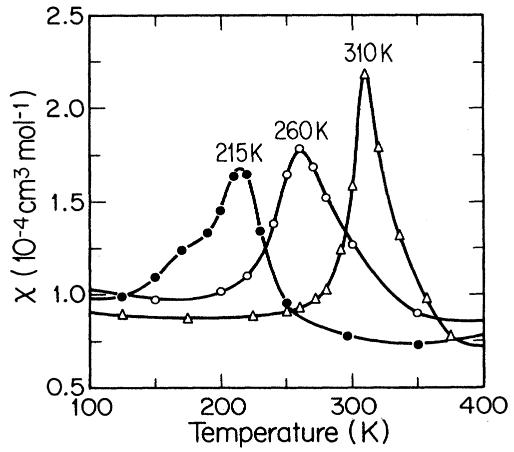

FIG. 1. Selected susceptibility data taken with a 5-kG field perpendicular to the $CuO_2$ planes. The curves are labeled by the peak which, from Ref. 7, is $T_N$. Note the double peak seen in the 215-K preparation, which is evidence for heterogeneity.

fusion coefficient is very large. After annealing at 725 °C the sample, which then had $T_N = 320$ K, broke apart, and no transport data for it will be presented.

Johnston *et al.*[9] have studied the dependence of the susceptibility peak on oxygen content and found that the peak temperature shifts to lower values with increasing oxygen content, going to zero at an excess oxygen concentration of $\sim 3\%$. Using their data, we find that our range of $T_N$ corresponds to excess oxygen concentrations of $\sim 0\%-1.5\%$. We assume here implicitly that the sample with the largest $T_N$ (320 K) is closest to being stoichiometric, that is, following Aharony *et al.*,[2] we assume that the diminution of the Néel temperature is caused by the presence of holes on the oxygen sites.

Figure 2 shows the conductivity $\sigma$ as a function of $1/T$ for (a) $T > 20$ K and (b) $T > 4$ K, for current in the $CuO_2$ sheets (*a-c* plane); Figs. 2(c) and 2(d) show analogous data for current perpendicular to the sheets, the orthorhombic *b* direction. We discuss the in-plane conductivity $\sigma_a$ first. Between 75 and 200 K [Fig. 2(a)] $\log\sigma_a$ appears to be nearly linear in $1/T$ corresponding to thermally activated behavior with a single activation energy. This activation energy decreases monotonically with increasing oxygen content, but it appears that all preparations have approximately the same prefactor, $\sim 45\ \Omega^{-1}\ \mathrm{cm}^{-1}$, which corresponds to $\sim 10^{-1}\ e^2/h$ per $CuO_2$ layer. There is a deviation from this simply activated behavior at the highest temperatures where the slope of $\log\sigma_a$ vs $1/T$ decreases. For $T \lesssim 50$ K, the temperature dependence of $\sigma_a$ becomes weaker with the differential activation energy decreasing monotonically with decreasing $T$. This behavior is typical of *variable-range hopping* in localized states near the Fermi energy. The data can be adequately fitted with the functional form expected[10] for hopping: $\sigma_0 \exp[-(T_0/T)^s]$ with $\frac{1}{4} < s < \frac{1}{3}$, encompassing three-dimensional hopping with or without carrier correlations and two-dimensional hopping. In our earlier measurements[6] on crystals with isotropic conductivity, we had seen hopping transport from 300 to 4 K, and could accurately determine $s = \frac{1}{4}$. The present experiment, however, shows hopping conductivity only below $\sim 50$ K, and this temperature range is too narrow to determine *s* very precisely. The magnitude of the hopping component is much more sensitive to oxygen content than that of the simply activated component. For the most reduced samples, the hopping conductivity is too small to measure with our highly resistive contacts. The hopping conductivity could not be measured for the most oxidized state below 30 K, either, since it becomes superconducting at lower temperature.

For $j \parallel b$ there is also a component with a single activation energy, although the activation energy is smaller than that of $\sigma_a$. The hopping component, although anisotropic by a factor 20–50, is manifest in both directions. This can be demonstrated by plotting the anisotropy of $\sigma$ as in Fig. 3. The anisotropy is quite weakly temperature dependent at low *T* indicating that the conductivity in this regime has approximately the same temperature dependence for both directions. However, the anisotropy increases dramatically when the simply activated component begins

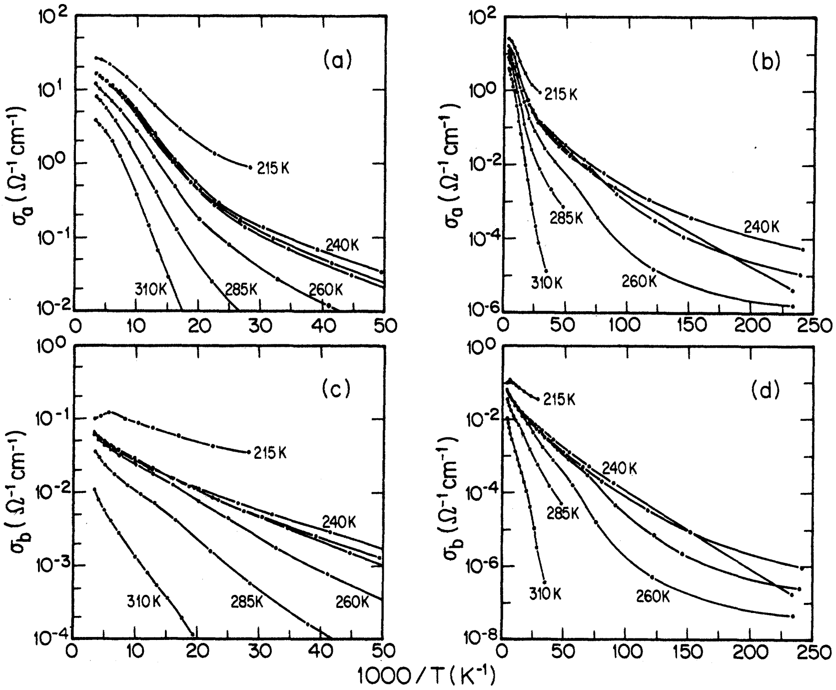

FIG. 2. Conductivity, measured by the Montgomery method, for various oxygen concentrations. The curves are labeled by $T_N$. (a) The in-plane conductivity $\sigma_a$ for $T > 20$ K, and (b) the full temperature range ($T > 4$ K). (c) and (d) The out-of-plane conductivity $\sigma_b$ in the same temperature ranges. Three different processing steps (see Table I) gave $T_N \approx 240$ K but show different conductivity at low *T*.

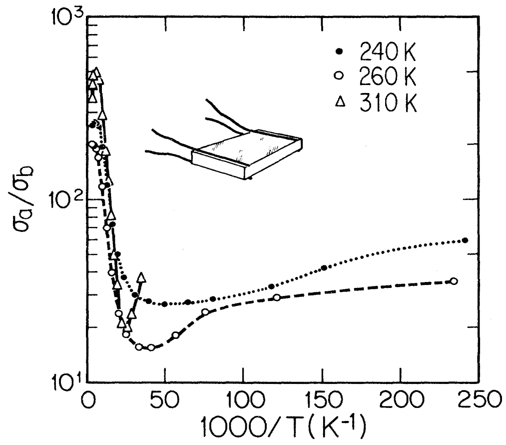

FIG. 3. Anisotropy of the conductivity as a function of $T$, obtained directly using Montgomery method.

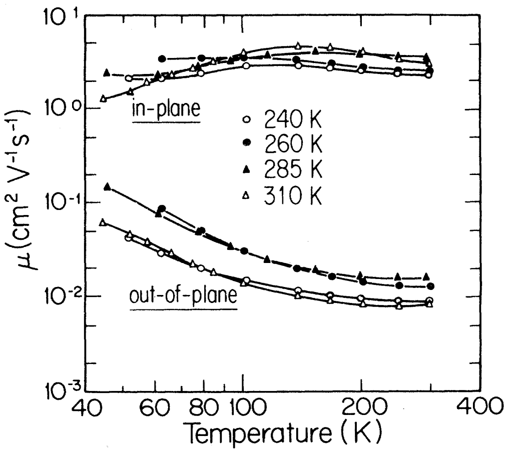

FIG. 5. The Hall mobilities for the in-plane (upper curves, $\mu_a$) and out-of-plane (lower curves, $\mu_b$) direction.

to dominate. It is striking, however, that despite the strong dependence of the anisotropy on temperature, it is only weakly dependent on oxygen concentration, even though the conductivities vary by orders of magnitude. The decrease at the highest $T$ is the result of the decreased slope of $\log\sigma_a$ vs $1/T$ mentioned above.

The change in the dominant transport process from simple activation to hopping at ~50 K is clear from the conductivity itself. Further evidence for this change in the transport process at ~50 K can be found in the Hall data. Figure 4 shows the Hall coefficient as a function of $1/T$ for $j \parallel a$. As usually found for $La_2CuO_4$ and other copper-oxide superconductors,[11] the Hall coefficient is positive. The simply activated component is seen here also at high temperatures with activation energies comparable to those for $\sigma_a$. The activation energies and prefactors are given in Table I. For the samples in which the hopping conductivity can be measured, there is a peak in the Hall coefficient at ~50 K. Such a peak was identified by Fritzsche,[12] in his classic studies of the insulator-metal transition in doped Ge, as the result of a crossover in the dominant conduction process from one with relatively high mobility and strongly $T$-dependent conductivity at high temperatures to another with lower mobility and weakly $T$-dependent conductivity at lower temperatures.

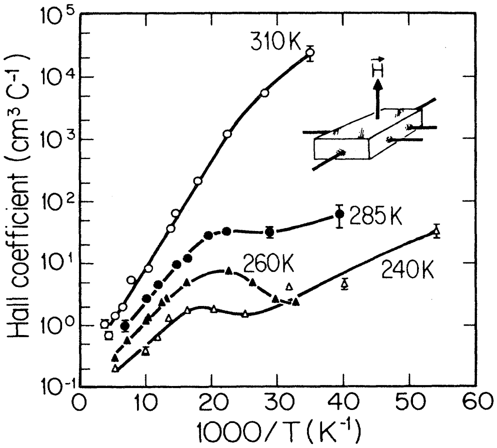

FIG. 4. Hall coefficient measured with an oscillating 6-kG field perpendicular to the $CuO_2$ planes and with current in the planes. Inset shows five-probe geometry for Hall measurements.

Because the Hall effect in $La_2CuO_4$ shows simply activated behavior at high temperatures with activation energy similar to that of $\sigma_a$, it is likely that it is the carrier density itself which is thermally activated. If that interpretation is correct, the product of $\sigma_a$ and $R_H$ gives the mobility in the $a$-$c$ plane. In Fig. 5 we have plotted this Hall mobility $\mu_a$ as a function of $T$ for the high-$T$ regime. For all preparations, but most clearly for the sample with $T_N = 310$ K, $\mu_a$ increases with $T$ at low $T$, reaches a peak at ~140 K and decreases at higher $T$. The decrease at high temperatures reflects the change in slope seen in $\log\sigma_a$ vs $1/T$ [Fig 2(a)] but not in $\log R_H$ vs $1/T$ (Fig. 4). Note that, like the anisotropy, the mobility is very weakly dependent on oxygen content, varying by only a factor ~2 while $\sigma_a$ varies by decades.

The weak dependence of the anisotropy on the oxygen content and the similarity of the activation energies of $\sigma_a$ and $\sigma_b$ suggest that the carriers which dominate the high-temperature conductivity in the two directions are the same. If true, this means the mobility in the direction perpendicular to the layers can be determined from the product of $\sigma_b$ and $R_H$. This quantity $\mu_b$ is also plotted in Fig. 5. This mobility is, like $\mu_a$, independent of oxygen content. Note that the variation by a factor ~2 is not systematic with $T_N$. The temperature dependence of $\mu_b$ is stronger than that of $\mu_a$ and has the opposite sign. At low $T$, the mobility perpendicular to the $CuO_2$ sheets, $\mu_b$, varies approximately as $T^{-2}$, but this temperature dependence saturates by ~150 K.

## IV. DISCUSSION

The positive Hall coefficient and thermopower[13] show that addition of oxygen gives rise to excess holes, so that oxygen, probably as an interstitial $O_2^-$ ion,[14] acts as an acceptor. As discussed in more detail below, there is little doubt that the low-temperature motion of the holes is by hopping. It is also clear that, at high temperatures, holes move by thermal activation to a set of highly anisotropic states. A variety of spectroscopies[15] indicates that excess holes reside primarily on the oxygen rather than on the Cu atoms. Thus, pure $La_2CuO_4$ is most simply described as a charge-transfer insulator[16] with a valence band arising primarily from O $p$ states and a conduction band arising primarily from Cu $d$ states. Obviously, these states are mixed because the bonding is strongly covalent, so the nature of the valence band in which the supercurrent carriers reside is quite complicated. It has even been proposed that an extra hole is bound to a $Cu^{2+}$ ion in a singlet state.[17]

The transport properties of $La_2CuO_{4+y}$ in the range $0 \lesssim y \lesssim 1.5\%$ can be generally understood using standard concepts in semiconductor physics.[18] Specifically, doped $La_2CuO_4$ exhibits properties which are in many ways similar to those of uncompensated Ga-doped Ge (Ge:Ga) near the insulator-metal transition. The properties of that system can be summarized as follows.[12]

The saturation regime, in which all impurities are ionized, occurs near room temperature. If the compensation (the ratio of donors to acceptors) is small the Hall coefficient is temperature-independent and gives the impurity concentration directly. As the temperature is lowered, one enters the regime in which the majority of carriers are bound to the impurities. The conductivity is first limited by the thermally activated fraction of the carriers which are ionized to the valence band, and both $R_H$ and $\sigma$ are simply activated with energy $\varepsilon_1$, the impurity binding energy. Note that the binding energy is not $2\varepsilon_1$ unless the compensation is extremely small.[18]

The temperature range in which impurity ionization can be observed is narrow, however, if the carrier concentration is high, and specifically if it is within a decade of the insulator-metal transition concentration. At these high dopant levels, impurity-band conduction dominates the higher mobility valence-band conduction as soon as a large enough fraction of the carriers are bound to the impurities. The onset of the new transport mechanism is signaled by a peak in $R_H$ and a smaller activation energy of $\sigma$. Actually, there are two thermally activated contributions to the impurity-band transport with energies $\varepsilon_2$ and $\varepsilon_3 < \varepsilon_2$. The energy $\varepsilon_2$ is that for excitation from a singly occupied impurity to the band of doubly occupied impurities. This is analogous to the correlation energy minus that bandwidth in the Hubbard model.[10] Because the doubly occupied states of the impurities are weakly bound, they are larger and overlap much more strongly than the ground states and form a band whose width increases with density. Thus $\varepsilon_2$ decreases rapidly with concentration, but the prefactor of this contribution is found[12] to be only weakly dependent on density.

At still lower temperatures, a second impurity-band mechanism takes over, again heralded by a peak in $R_H$. This component arises from thermally assisted tunneling (hopping) between localized states near the Fermi energy, $E_F$. This component of $\sigma$ is simply activated at the highest temperatures at which it is observed, because it is dominated by hopping between nearest neighbors. As the temperature is lowered, however, it crosses over to variable-range-hopping. The prefactor of the hopping component depends exponentially on the density, because it involves tunneling between impurities, and it depends strongly on the compensation ratio, because carriers can hop only between singly occupied and empty states. The energy $\varepsilon_3$, however, depends only weakly on concentration.[12]

The separation of the three components of $\sigma$ is obvious when the impurity density is much less than $n_c$, the critical concentration for the IMT. However, for densities within about a decade of $n_c$ the distinction is blurred. In this range, the doubly occupied impurities, which are only weakly bound, give rise to a tail of states on the edge of the valence band, making the distinction between transport in these two types of states less clear. At the same time, the energy $\varepsilon_2$ becomes small and the prefactor of the hopping component becomes large so that the temperature range in which $\varepsilon_1$ can be identified becomes very narrow.

We now apply these concepts to our measurements in $La_2CuO_{4+y}$. We see no temperature range corresponding to the saturation regime in which $\sigma$ and $R_H$ are independent of $T$. However, as discussed next, the binding energy of the impurities is larger than in Ge, and this would shift the extrinsic region to higher temperature. Furthermore, even in Ge:Ga the extrinsic range is narrow at concentrations close to the IMT, like those we have in $La_2CuO_{4+y}$.

The most straightforward interpretation of the regime at high temperatures in Figs. 2(a), 2(c), and 4, in which $\sigma_a$, $\sigma_b$, and $R_H$ are simply activated, is that it is the impurity-ionization regime. If this interpretation is correct, the ionization energy is best estimated from the activation energy of $R_H$ for the most lightly doped state with $T_N = 310$ K, because, as in Ge:Ga, $\varepsilon_1$ decreases as the critical concentration for the IMT is approached. This is only a lower bound, however, because the energy does not appear to have saturated even at $T_N = 310$ K. As seen in Table I, this estimate gives about 35 meV for the ionization energy. This value is $\sim 3$ times higher than that for acceptors in Ge. The dielectric constant in the photon-energy range near 30 meV is[19] $\sim 20$ in $La_2CuO_4$, similar to the value of 16 in Ge. The effective mass of heavy holes in Ge is $\sim 0.3$; differences in mass could easily be enough to account for the difference in binding energy.

We cannot determine the impurity concentration from $R_H$ because it does not saturate at high temperatures. However, if the activated region corresponds to impurity ionization, the density must be higher than the room-temperature value of $1/eR_H$, and it is usually smaller than the infinite temperature extrapolation of $1/eR_H$. Both of these values are given in Table I, along with an estimate of the density of excess oxygen from the susceptibility data of Johnston *et al.*[9] To make the latter estimate we scaled our highest $T_N$ to that of Johnston *et al.*, and assumed that $T_N$ saturates at its highest value in the limit of zero excess oxygen. It is clear that the hole density estimated from the Hall effect and the oxygen excess are in very reasonable agreement, given the uncertainties of this procedure. Note that the charge state of the excess oxygen is not definitely known;[14] however, Schirber *et al.*[14] suggest the excess oxygen is present as $O_2^-$. In this case, the hole concentration is $\frac{1}{2}$ the excess oxygen concentration, further improving the agreement. It is surprising that the prefactor of $R_H$ scales inversely as the acceptor density, $N_A$. In the absence of compensation, when there is no hopping conductivity and the ionization energy is $2\varepsilon_1$, the prefactor is expected[18] to go as $(N_A)^{1/2}$. On the other hand, if there is a fixed compensation ratio, the prefactor is independent of $N_A$.

As expected for a doped semiconductor, the mobilities (Fig. 5) are only weakly dependent on dopant density, even though $\sigma$ and $R_H$ vary rapidly with the change in the Néel temperature. In addition, the decrease of $\mu_a$ at high temperature is weak enough to be accounted for by scattering from phonons or magnetic excitations. The much lower mobility in the $b$ direction is consistent with the much smaller dispersion of the bands[20] in this direction. The temperature dependence of $\mu_b$ is similar to that found[21] in a variety of molecular crystals. In these, the reduction of the mobility as the temperature is increased comes from phonon scattering. In fact, in the limit in which the bandwidth is less than $kT$, Friedman[22] found that the carrier velocity is independent of $T$, and that, with a scattering rate proportional to the phonon density $\sim T$, the diffusion coefficient goes as $T$. The Einstein relation then gives $\mu \sim T^{-2}$, just as we find for $\mu_b$. The saturation at high temperatures would result when the mean free path is reduced to the size of the lattice constant or when phonon-assisted hopping begins to dominate.[21]

Although in some respects the behavior of the mobility is consistent with impurity ionization, some aspects are disturbing. In particular, $\mu_b$ is only $\sim 10^{-2}$ cm$^2$/Vs at saturation (Fig. 5), whereas in molecular crystals saturation occurs[21] for $\mu \sim 1$ cm$^2$/Vs. The latter have intermolecular hopping matrix elements only of order meV, and it would be surprising if the matrix elements in $La_2CuO_4$ were even smaller. It is still more surprising that the in-plane Hall mobility is so small. With an effective mass equal to that of the free electron, the mobility ($\sim 3$ cm$^2$/Vs) corresponds to a mean free path of the order of the lattice constant. Of course, a higher effective mass might explain the low mobility. Coupling of the motion of the excess holes to the antiferromagnetic background is expected to lead to such a mass enhancement.[23] Indeed, there is no adequate theory of the Hall effect in such a situation, so the low Hall mobility may not be simple to interpret.

One alternative interpretation of the simply activated behavior is that the activation energy measured is $\varepsilon_2$, that is, the energy for excitation from a singly occupied impurity to a band of doubly occupied impurities. $\varepsilon_2$ decreases more rapidly than $\varepsilon_1$ near the IMT. Then $\varepsilon_1$ might be larger, consistent with an enhanced mass.

Another explanation is that disorder, from sources other than the impurities, creates a tail of localized states on the valence band even at densities well below $n_c$. The activation energy of the conductivity would then be the energy difference between $E_F$ and the mobility edge in the valence band. This is the situation in amorphous semiconductors. The conductivity is thermally activated, and the Hall mobility, of order 1 cm$^2$/Vs, is essentially temperature independent.[10]

If $E_F$ lies in a band tail and moves into the band with increasing density, then the IMT in $La_2CuO_{4+y}$ should be similar to that in Si metal-oxide-semiconductor field effect transistors (MOSFET's).[24] In that case $\sigma$ shows behavior qualitatively similar to that in Fig. 2(a), albeit with a prefactor $\sim e^2/h$, as expected theoretically.[25] In $La_2CuO_4$ we measure a prefactor of $\sigma_a$ about 10 times smaller than this per $CuO_2$ layer. The Hall mobility in MOSFET's is not yet understood. It is found to be thermally activated with energies of the same order as those deduced from the conductivity. Equivalently, $R_H$ in MOSFET's is independent of $T$, whereas that in $La_2CuO_4$ is thermally activated.

In measurements reported earlier,[6] we found no clear evidence of simply activated transport at high $T$. Rather, the conductivity was limited by hopping at all temperatures. As already mentioned, the difference between the earlier results and those presented here are primarily the consequence of sample-to-sample variations. In particular, as can be seen from Fig. 2, the magnitude of the hopping component depends strongly on hole concentration, as it does in Ge:Ga. Indeed, even the three preparations which have nearly indistinguishable Néel temperatures have very different hopping conductivities at low $T$.

Although the hopping is anisotropic in the sample studied here, the conductivities $\sigma_a$ and $\sigma_b$ differ by less than a factor of 50, and the anisotropy is only weakly temperature dependent. This suggests that the percolation network, necessary for hopping conduction, is not completed in a single layer, and a few hops in the $b$ direction occur even when current is measured in the $a$-$c$ plane. Of course, current in the $b$ direction requires many more hops between planes, but the temperature dependence of these is probably not much stronger than those which limit the current in the $a$-$c$ plane.

## V. CONCLUSIONS

The conductivity, its anisotropy, and the Hall effect all provide clear evidence of a change in the transport mechanism in the temperature range 20–50 K for all the oxygen concentrations studied. The conductivity shows simply activated behavior at high $T$, but is characterized by a continuously varying activation energy at low $T$. The anisotropy increases with $T$ at high $T$, but is weakly dependent on $T$ at low $T$ with a minimum in the crossover region. The Hall coefficient is simply activated at high $T$, but has a weaker temperature dependence at low $T$ and has a maximum in the crossover region.

The low-temperature conductivity is apparently limited by thermally assisted tunneling between localized states. The strong dependence of the prefactor of this component on impurity concentration and the peak in the Hall coefficient are features which characterize the onset of this process in impurity-band conduction in conventional semiconductors.

The origin of the high-temperature process is less clear. The observation that the Hall coefficient has an activation energy similar to that of the conductivity and that the mobilities extracted from the product of $\sigma$ and $R_H$ are very weakly dependent on oxygen content shows that the high-temperature component arises from thermal excitation of carriers from the Fermi level to states with higher energy and higher mobility. The mobilities parallel and perpendicular to the $CuO_2$ planes are very different, both in magnitude and temperature dependence. As a result, the anisotropy of the conductivity is strongly temperature dependent, reaching a maximum of $\sim 500$ near 150 K.

The origin of these states is not, however, obvious. On the one hand, the qualitative similarity between $La_2CuO_{4+y}$ and Ge:Ga and the agreement between the carrier density estimated from the Hall effect and the oxygen excess suggests that the states at $E_F$ arise from the excess oxygen, as proposed by Moshchalkov.[26] The transport might then occur by excitation to a band characterized by a large mass. On the other hand, the low mobilities suggest that the transport may involve states near a mobility edge. The disorder causing such localization might also come from interstitial excess oxygen. In fact, the transport states might be doubly occupied impurity sites.

Alternatively, the disorder may have a different source, such as vacancies in the $CuO_2$ planes, which would create a tail of localized states on the valence band even in the absence of excess holes. The hopping conductivity makes it clear, in any case, that disorder plays an important role in the insulator-metal transition. Perhaps the nature of the states in which the high-temperature transport takes place will be clarified by measurements on still more lightly doped and more defect-free crystals.

While this work was being prepared for submission, we learned of closely related work by Cheong *et al.*[27] on a single crystal of $La_2CuO_{4+y}$.

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[*] Also at Department of Physics, Massachusetts Institute of Technology, Cambridge, MA 02139.

[†] Permanent address: Defense Science Technology Organization, Adelaide, Australia.

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