Frequency Dependence of the Conductivity and Dielectric Constant of La_2CuO_{4+y} near the Insulator-Metal Transition

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Measurements are reported of the conductivity and dielectric constant at frequencies up to 10 MHz for a single crystal of La_2CuO_{4+y} with $y \sim 0.001$ to 0.01. The reported behavior is typical of conventional doped semiconductors, with dielectric constant (at $y=0$) and effective mass that are not exceptionally large. The dielectric constant grows as the insulator-to-metal transition is approached, but only for the electric field in the CuO_2 layers, indicating that the transition is two dimensional. The crossover to weak localization occurs close to the antiferromagnetic phase boundary.

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The elucidation of the mechanism of high-temperature superconductivity[1] will require a deeper understanding of the highly correlated behavior of electrons in the lamellar copper oxides. These correlations give rise to antiferromagnetism[2] and insulating properties[1] when the density of holes in the CuO_2 layers is very low. However, a few percent excess holes is sufficient to destroy the magnetic long-range order[3] and cause an insulator-to-metal transition (IMT). It is widely believed that a complete explanation of the superconductivity will require a correct description of the IMT. However, quite different views of the transport properties in the lightly doped regime have appeared in the literature. For example, recently, measurements were reported[4] of the ac conductivity and dielectric constant of lightly doped La_2CuO_4 in the frequency range 3–90 GHz. Interpreting these results, the authors concluded that the holes have an extremely large effective mass ($m^* = 1100 m_e$) and that the undoped material has an unusually large dielectric constant (50–75). Such properties are very different from those of conventional doped semiconductors. On the other hand, we have reported a study[5] of the conductivity and Hall effect of a particular single crystal of La_2CuO_{4+y} whose hole concentration was varied by annealing it in various partial pressures of oxygen. We found that the behavior of La_2CuO_{4+y} with increasing y was in most ways similar to that of doped semiconductors on approaching the IMT from the insulating side.

In this Letter we report measurements of the ac conductivity and dielectric constant from 1 kHz to 10 MHz for the *very same* single crystal on which the Hall effect and conductivity were measured.[5] These properties, like the dc transport, show behavior similar to that of conventional semiconductors: The ac conductivity follows a power-law frequency dependence with an exponent that decreases with increasing temperature and impurity concentration. The dielectric constant appears to diverge as the IMT is approached, which is why very large values are sometimes reported. We find values of the effective mass and the dielectric constant, in the absence of impurities, that are not exceptionally large. One feature of the IMT is, however, definitely unconventional: the IMT is two dimensional (2D) with no measurable increase of the dielectric constant when the electric field is perpendicular to the CuO_2 layers. Such a clear manifestation of a 2D Mott-Anderson transition in a doped semiconductor has not been previously reported.

The single-crystal growth, control of oxygen content, and characterization are discussed in Ref. 5. After each annealing step, in oxygen or argon, measurements were made of the ac conductivity and dielectric constant, in addition to the magnetic susceptibility, dc conductivity, and Hall effect.[5] We use the Néel temperature T_N to label the state of the crystal, since T_N decreases monotonically with y.

As for conventional doped semiconductors, the Hall coefficient and conductivity are thermally activated at high temperature, presumably because the carrier density is limited by the ionization of holes bound to acceptors. The binding energy is estimated to be about 40 meV from the activation energy for the preparation with the lowest value of y. At low temperatures, just as for doped Ge or Si, the conductivity and Hall effect show clear evidence of the crossover to hopping (phonon-assisted tunneling) in the impurity band. Our ac measurements are all made at these low temperatures where the holes are bound to the acceptors.

The real and imaginary parts of the ac conductivity were determined using a 50-Ω metal-film load resistor in series with the sample, and measuring the current and voltage with lock-in amplifiers. To make electrical contact, the two surfaces normal to the field direction were completely covered with silver paint. Our experience is that such contacts have large dc resistance. However, because of the small thickness of the high-resistance region, the contact has a large capacitance and does not contribute significantly to the impedance.

Figure 1(a) shows the ac conductivity σ as a function of frequency ω for $\mathbf{E}\|\mathbf{a}$ for various preparations labeled by T_N. In orthorhombic notation, space group *Cmca*, **a** is parallel to the CuO_2 layers and is indistinguishable from **c** because of twinning. It is apparent that σ increases as a power law, ω^s, for each preparation but that the exponent s decreases with increasing oxygen content, that is, with decreasing T_N. The magnitude of σ at fixed ω increases with oxygen content. Figure 1(b) shows $\sigma(\omega)$ for the preparation with $T_N = 285$ K at various temperatures. As T is increased s becomes smaller, and at 4.2 K it is close to 0.8.

The power-law frequency dependence of the conductivity is characteristic of tunneling of electrons between localized states within kT of the Fermi energy. This behavior was first seen by Pollak and Geballe[6] in doped Si, and is common to a wide variety of disordered materials. The power law arises from the distribution of tunneling rates, which is enormously broad because it depends exponentially on a random variable, the distance between the localized states. When the density of impurities and the temperature are low enough that tunneling between isolated pairs of sites dominates, the conductivity is predicted to follow[6] $\sigma(\omega) \sim \omega R_\omega^4$, where R_ω is the pair separation. Because the tunneling rate is exponential in the separation, one has $R_\omega \sim \ln(\omega_0/\omega)$, which in turn leads to $\sigma(\omega) \sim \omega[\ln(\omega_0/\omega)]^4$; this empirically simulates an ω^s behavior with $s = 0.8$ over a large range of frequencies. This is the value of s observed[6] in lightly doped Si. At elevated temperatures, the number of pairs with separation R_ω and energies separated by less than kT becomes temperature dependent and the dependence of $\sigma(\omega)$ on R_ω changes because multipole hops begin to contribute; this is the reason for the observed decrease of s with T. This reduction of s happens at lower temperature for higher-impurity concentration, while the magnitude of σ at fixed ω increases with concentration. Thus, the behavior seen in Fig. 1 is the same as that found in conventional doped semiconductors.

In Fig. 2, the real part of the dielectric function, $\epsilon_1(\omega)$, for $\mathbf{E}\|\mathbf{a}$ and $\mathbf{E}\|\mathbf{b}$ is plotted for various preparations. The power-law decrease of the dielectric constant at low frequency has the same origin as the ac conductivity in Fig. 1. Since $\sigma \sim \omega^s$, the Kramers-Krönig (KK) relations require that the imaginary part of the conductivity, $\omega\epsilon_1$, also follows ω^s. The KK relations further require that the ratio of the imaginary to the real part of σ be equal to $\tan(s\pi/2)$. When the data of Fig. 2 are fitted with the sum of a power law plus a constant, we find that these relations are obeyed for all T_N and T showing that the power-law dependence of ϵ_1 at low frequency comes from hopping and that our fitting procedure is valid. We find that the ac conductivity is anisotropic, being about 10 times larger for $\mathbf{E}\|\mathbf{a}$ than for $\mathbf{E}\|\mathbf{b}$, but the anisotropy is independent of frequency. By comparing Figs. 2(a) and 2(b), it can be seen that, as required by the KK relations, the anisotropy in $\epsilon_1(\omega)$ is also frequency independent at low ω: The magnitude of ϵ_1 at low ω and the exponent s change in the same way with oxygen content for $\mathbf{E}\|\mathbf{a}$ and $\mathbf{E}\|\mathbf{b}$.

For each preparation of the crystal, and for each polarization, the dielectric constant approaches a constant value at high frequency. The dependence of ϵ_a and ϵ_b (the high-frequency values for $\mathbf{E}\|\mathbf{a}$ and $\mathbf{E}\|\mathbf{b}$, respectively) on acceptor density provides the most striking results of this work. To extract quantitative information from the data we need an estimate of the acceptor density. Recent measurements suggest that the Hall coefficient, which is thermally activated[5] at low T, saturates near room temperature, so its value at 300 K gives a good estimate of the acceptor density directly. The acceptor density, estimated in this way, and the oxygen determined from weight loss agree[5] if one divides the latter by 2, since the acceptors are probably O_2^-.

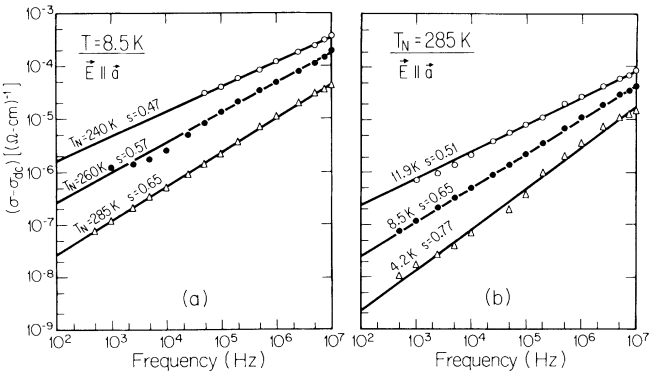

FIG. 1. Conductivity of La_2CuO_{4+y} vs frequency on double-logarithmic plots for $\mathbf{E}\|\mathbf{a}$ and for (a) several y characterized by the Néel temperature T_N and (b) several temperatures for the preparation with $T_N = 285$ K. The solid lines are least-squares fits to $\sigma(\omega) = \sigma_0\omega^s$, and the values of s from the fits are given for each line.

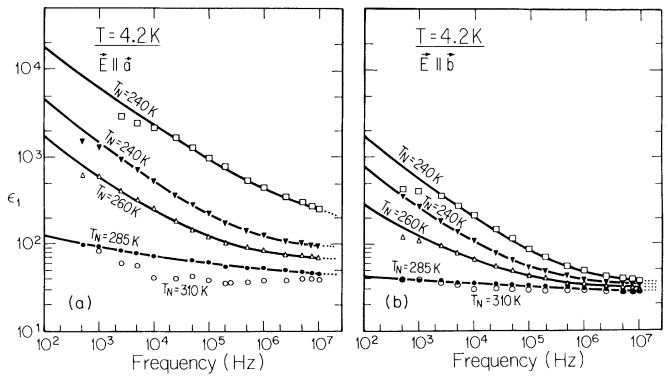

FIG. 2. Dielectric constant of La_2CuO_{4+y} vs frequency on double-logarithmic plots of several y characterized by T_N for (a) $\mathbf{E}\|\mathbf{a}$ and (b) $\mathbf{E}\|\mathbf{b}$.

In Fig. 3 we show ϵ_a and ϵ_b as functions of the acceptor concentration, N_A. ϵ_a appears to be diverging at a critical value of $N_A \leq 10^{20}$ cm^{-3}, whereas ϵ_b is independent of N_A to within experimental error. Before examining this behavior, we note that the dielectric tensor of undoped La_2CuO_4 is nearly isotropic. The anisotropy for the most reduced sample is only $\epsilon_a/\epsilon_b \sim 1.25$, and extrapolation to zero hole density gives $\epsilon_a/\epsilon_b \sim 1.1$. The diagonal elements of the dielectric tensor of undoped La_2CuO_4 obtained in this way are 30 ± 3 and 27 ± 2 in the a and b directions, respectively. These are comparable to values found for PbO, BaO, and CuO, and are not, therefore, unusually large. It is thus clear that the very large and anisotropic dielectric constants reported[4,7] for La_2CuO_4 arise not from the phonons, as previously believed, but rather from the excess holes.

In Fig. 4 $(\epsilon_a - \epsilon_h)^{-1}$ is plotted against N_A, where ϵ_h, the value of ϵ_a extrapolated to $N_A = 0$, is the dielectric constant of the host, La_2CuO_4, with no holes. The behavior for $\mathbf{E} \| \mathbf{a}$ is qualitatively similar to that[8] in phosphorus-doped Si for which the inverse dielectric constant goes to zero linearly at the critical density of the IMT. A critical density cannot be determined for La_2CuO_{4+y}, but the dielectric constant begins to diverge well before T_N goes to zero. This is seen clearly in the inset of Fig. 4, where $(\epsilon_a - \epsilon_h)^{-1}$ is plotted against T_N.

The polarizability α of an isolated acceptor may be obtained from the slope of ϵ_a vs N_A at low density (Fig. 3). The value of α can then be used to estimate the size of the wave function of the hole bound to the acceptor. For a 3D hydrogenic orbit the effective-mass approximation gives[8] $\alpha = \frac{9}{2} \epsilon_h a_0^3$, where a_0 is the effective Bohr radius. The explicit numerical coefficient will be different for the highly anisotropic wave functions in La_2CuO_4, but this will not have great impact on the value of a_0 because the coefficient enters only to the $\frac{1}{3}$ power. We find, in this way, that $a_0 = 8 \pm 2$ Å for the radius in the CuO_2 plane. For $\mathbf{E} \| \mathbf{b}$ the polarizability of the acceptors is too small to measure; this places an upper bound of 3 Å on the extent of the hole charge distribution perpendicular to the layer. We conclude that the holes are confined to a single CuO_2 layer.

From Fig. 4 the in-plane electric susceptibility appears to diverge at a 3D critical density of acceptors $n_3 \sim (4\text{-}8) \times 10^{19}$ cm^{-3}. Using $a_0 = 8 \pm 2$ Å, one finds values of $n_3^{1/3} a_0 \sim 0.3$, in good agreement with the Mott criterion, 0.26 ± 0.05, found for the impurity-band IMT in a wide variety of materials. Recently, Serre, Ghazali, and Gold[9] have argued that for 2D the Mott criterion is $n_2^{1/2} a_0 \sim 0.15$, also in good agreement with our result.

Our value of a_0 is consistent with the observation that the magnetic long-range order is destroyed at a low density of excess holes. An orbit with 8-Å radius has as many as ~ 15 frustrated bonds on its perimeter. This is enough, using the model of Aharony *et al.*[10] together with the simulations of Vannimenus *et al.*,[10] to account for the fact that antiferromagnetic long-range order is destroyed at a hole concentration of $\sim 2\%$.

Using a hydrogenic model for the acceptors, the product of the radius (8 ± 2 Å) and the binding energy (40 meV) gives a host dielectric constant (25 ± 6) in good agreement with the value measured directly (see Fig. 3). The same model yields an effective mass $m^* = (2 \pm 1) m_e$, much smaller than the value reported in Ref. 4 but of the same order as values obtained from penetration depth and optical measurements[11] on superconducting copper oxides.

The origin of the unusually large mass reported in Ref. 4 is the low mobility, $e^2\tau/m^* = 3$ cm^2/Vs, which we measure in our crystals as well.[5] The question is wheth-

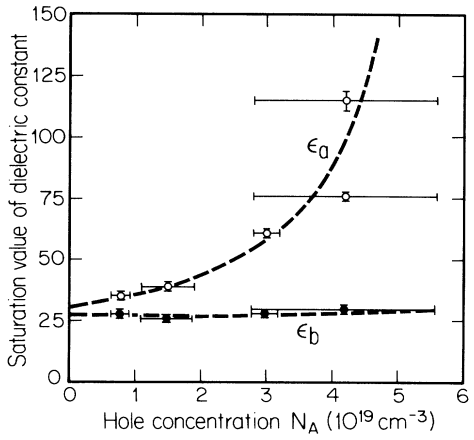

FIG. 3. Dielectric constant as a function of acceptor density for $\mathbf{E} \| \mathbf{a}$ and $\mathbf{E} \| \mathbf{b}$. The density was determined from the room-temperature value of the Hall coefficient. The dashed curves are guides to the eye.

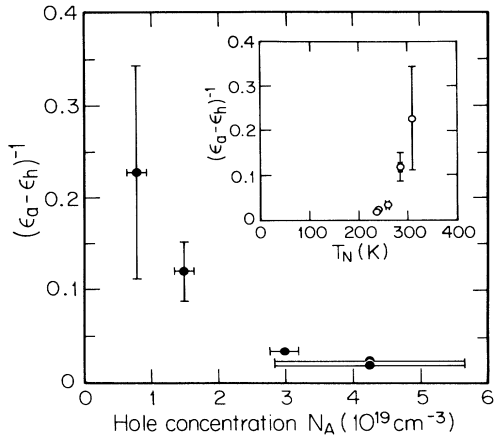

FIG. 4. The inverse of the contribution of the impurities to the dielectric constant vs acceptor density for $\mathbf{E} \| \mathbf{a}$. The host dielectric constant ϵ_h was taken to be 30 ± 3 from Fig. 3. Inset: The same quantity vs T_N.

er, as proposed in Ref. 4, $\tau \sim 10^{-12}$ s and $m^* \sim 1000 m_e$, or whether m^* is smaller and τ is shorter. Our value of $m^* \sim 2m_e$ implies $\tau \sim 10^{-14}$ s. If this is correct then the broad maximum in the conductivity reported in Ref. 4 must have some explanation other than the large τ. A scattering time of $\sim 10^{-14}$ s is consistent with the idea that the holes move through the dense, rapidly fluctuating spin system of the Cu ions which have $h/J \sim 10^{-14}$ s. The broad peak reported by the authors of Ref. 4 is difficult to understand in terms of their own model because the pinning energy extracted from the ac conductivity is 3 orders of magnitude smaller than the activation energy measured in their ac and dc conductivity.

As emphasized above, the behavior of the ac conductivity and dielectric constant on the insulating side of the IMT is, in many ways, similar to that in conventional doped semiconductors. However, several features of the IMT in La_2CuO_{4+y} are quite different from those in Si and Ge. The IMT in La_2CuO_{4+y} is 2D rather than 3D in character. This means that the growth of the dielectric constant, while indicating a rapid increase of the localization length, is not a true divergence, because in two dimensions at $T=0$, all states are localized. The localization length is predicted[12] to grow exponentially with the conductance, just as the antiferromagnetic correlation length grows exponentially with T^{-1} above the 3D Néel temperature. Since the electric susceptibility, $(\epsilon_a - \epsilon_h)/4\pi$, is proportional to a power of the localization length, it should also grow exponentially with the conductance. One expects, therefore, not a true phase transition but rather, at finite T, a continuous evolution from strong to weak localization. Thus, when the conductivity exceeds e^2/h per layer one expects logarithmic corrections to the conductance which have magnitude e^2/h per layer. We have, indeed, shown[13] that the conductivity in a variety of $La_{2-x}Sr_xCuO_4$ crystals can be described in this way. Specifically, samples in the spin-glass region of the phase diagram between the Néel and superconducting regions are better characterized as weakly localized 2D metals rather than semiconductors.

In conclusion, we have found that the IMT in La_2CuO_{4+y} provides a beautiful example of a Mott-Anderson transition in a 2D doped semiconductors. We have shown that the dielectric constant in the absence of excess holes is not unusually large, but that the large values often reported are the result of the rapidly increasing localization length as the IMT is approached. A simple hydrogenic model describes the impurities, but only if the effective mass is $\sim 2m_e$, a value that is not unusually large. Contrary to what has been generally believed, the IMT, where there is a gradual crossover from strong to weak localization, occurs close to the phase boundary of the antiferromagnet, rather than that of the superconductor. Indeed, the dielectric constant becomes very large at hole densities low enough that the magnetic long-range order is still preserved. The discovery that the IMT is two dimensional opens new avenues of research in the physics of the lamellar copper oxides. In particular, magnetoresistance measurements in the weak-localization domain are already underway.

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