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Resistivity of nonmetallic $La_{2-y}Sr_yCu_{1-x}Li_xO_{4-\delta}$ single crystals and ceramics

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The resistivity of nonmetallic $La_{2-y}Sr_yCu_{1-x}Li_xO_{4-\delta}$ single crystals and ceramics accurately follows the functional form $\exp((T_0/T)^{1/4})$, characteristic of variable-range hopping. For each of the crystals grown from Li-containing flux and CuO flux, pure reduced ceramics, and ceramics containing 0.025 to 0.2 mole% Li, the values of T_0 are in the range $0.3-7\times10^6$ K. The hopping conductivity shows that the crystals, which also manifest the two-dimensional quantum spin fluid state, antiferromagnetism, and the tetragonal-to-orthorhombic transition, are nonmetallic because the electronic states at the Fermi energy are localized. No evidence of a large gap is observed, and all samples, including the reduced ceramic, are p type, leading to the suggestion that in the nonmetallic state as well as the superconductor, the Fermi energy lies near the top of the band of singly occupied states (lower Hubbard band). The suppression of superconductivity by Li impurities is discussed.

I. INTRODUCTION

The materials $La_{2-y}Sr_yCuO_4$ and $YBa_2Cu_3O_{7-\delta}$ are unusual superconductors not only because their transition temperatures (T_c's) are so high,[1,2] but also because their superconducting transition occurs in close proximity to other kinds of phase transitions. $La_2CuO_{4-\delta}$ has structural[3] tetragonal-to-orthorhombic (T-O), antiferromagnetic,[4] and metal-nonmetal phase transitions at temperatures which are extraordinarily sensitive to oxygen and impurity content. It seems clear that clues to the origin of the high T_c's will come from studies of these other phase transitions. In particular, the discovery[5] in the nonmetallic phase of La_2CuO_4 of a new magnetic state, the two-dimensional (2D) quantum spin fluid (QSF), with a very high-energy scale for magnetic excitations, lends credence to theories[6] in which the superconductivity, the magnetism, and the nonmetallic state have a common origin in the Coulomb interaction between the valence electrons. Understanding, in detail, the nature of the nonmetal is therefore very important.

In this paper we report measurements of the resistivity of La_2CuO_4 single crystals and ceramics, most of which are nonmetals. The crystals are the same as those which were used in studies of the QSF state and the T-O transition. Surprisingly, we find no case in which the resistivity is high because of a large energy gap, as expected for a Mott insulator. Rather, the resistivity is high because the current is limited by thermally activated hopping at the Fermi energy.

II. EXPERIMENTAL DETAILS

A complete discussion of the crystal-growth technique will soon be published;[7] therefore, a brief description will suffice for the present. The crystals were grown from a flux containing approximately 50 mole% each of $Li_4B_2O_5$ and $Sr_yLa_2CuO_4$ with y in the range 0.2 to 2, prepared from La_2O_3, CuO, $SrCO_3$, and B_2O_3. The melt was seeded with a Pt wire at ~1425 K and, with very low cooling and pulling rates, platelike crystals were obtained with dimensions as large as $15\times20\times1$ mm^3, the smallest dimension was along the orthorhombic b (tetragonal c) axis. Some small crystals were also obtained using a similar technique but with CuO as the flux.[8]

Both because of its intrinsic interest and also because Li is almost certainly incorporated into the crystals if present in the flux, we have studied the effect of Li addition on the resistivity of ceramic La_2CuO_4. To prepare ceramics, La_2O_3, CuO, and Li_2CO_3 powders were heated repeatedly in a covered platinum crucible at 1275 K for ~10 h with grindings between heat treatments until single-phase ceramics of the orthorhombic or tetragonal La_2CuO_4 structure were obtained. Pressed pellets were heated to 1375 K for ~5 h in air and then allowed to cool gradually in the furnace. The pure ceramics, containing no Li, were subjected to a variety of heat and oxygen treatments.

Electrical contact was made to all samples with silver paint. For the single crystals, however, such contacts were found to have very high resistance, on the order of kΩ at room temperature. Consequently, for the crystals, contacts were baked at 675 K in air for 30 min resulting in a substantial decrease of the contact resistance.[8] The samples were placed in He vapor in a variable-temperature cryostat, and both the four-probe and two-probe resistance were measured from room temperature to ~2 K. Because most of our samples are nonmetals with very strongly temperature-dependent resistance, special care was taken to establish a constant temperature for each resistance measurement. In every measurement, the applied voltage was kept low enough that the four-probe voltage was proportional to the current.

III. RESULTS

A. Variable-range hopping

Figure 1 shows the resistivity of three single crystals of La_2CuO_4 grown from Li flux, two of which are nominally pure but undoubtedly contain some Li and one of which

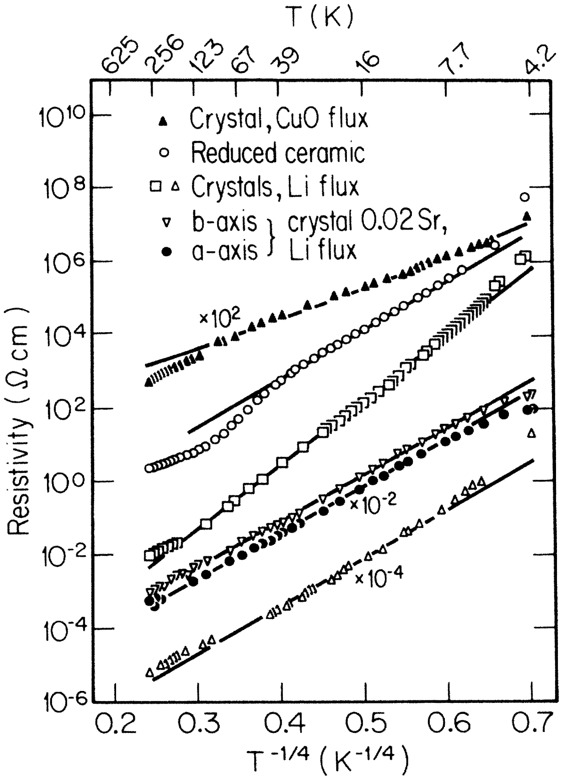

FIG. 1. Resistivity for (from top to bottom) a pure crystal of La_2CuO_4 grown from CuO, a reduced ceramic, a crystal grown from Li flux, the *b* and *a* orthorhombic directions for a crystal of $La_{1.98}Sr_{0.2}CuO_4$, and a second crystal from Li flux. The data are plotted against $T^{-1/4}$ to show the remarkable agreement with the VRH form. The solid lines are least-squares fits to Eq. (1) with the exponent $\nu = 0.25$. Susceptibility measurements show that the CuO-grown crystal orders magnetically at ~160 K.

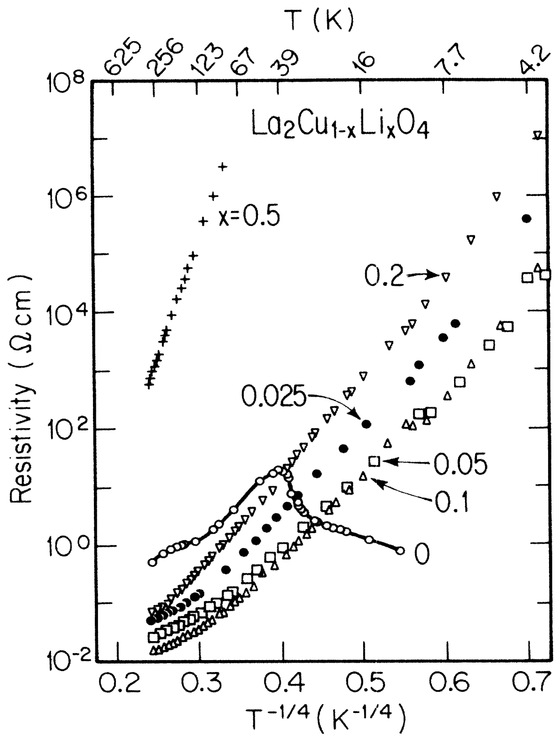

FIG. 2. Resistivity vs $T^{-1/4}$ for Li-containing ceramics. The $x = 0$ sample reaches zero resistance near 2 K. Between $x = 0.025$ and $x = 0.2$ the VRH conductivity is quite insensitive to x (see Table I for fitting parameters). Notice that at room temperature the resistivity decreases with Li addition up to $x = 0.1$ but then increases rapidly.

contains, in addition, a small amount of Sr. Also plotted are the resistivity of a sample of pure ceramic which was reduced in a flow of argon at 675 K for $\frac{1}{2}$ h and a crystal grown from CuO flux. The data are offset, as indicated, to make them visible. Note that measurements were made both along the orthorhombic *b* and *a* (or *c*) axes for the Sr-doped sample, but there is no anisotropy to within the accuracy of our measurement of the absolute resistivity. The latter is limited by our ability to determine the geometrical factors for our odd-shaped crystals.

The logarithm of the resistivity is plotted against $T^{-1/4}$ in Fig. 1 to illustrate the impressive agreement between the data and the Mott variable-range-hopping (VRH) law. Least-squares fitting of the data to the form[9,10]

$$\rho = \rho_0 (T/T_0)^{1/2} \exp((T_0/T)^{\nu}) \tag{1}$$

gave values of the exponent in the range $\nu = 0.25 \pm 0.05$. The weakly temperature-dependent prefactor has negligible influence on the value of ν. The solid curves shown in Fig. 1 are the results of fits with fixed $\nu = 0.25$.

Figure 2 illustrates the effect of Li addition on the resistivity of ceramics. Samples of $La_2Cu_{1-x}Li_xO_4$ were prepared with $x = 0.00$, 0.02, 0.05, 0.1, 0.2, and 0.5. The sample with no Li is metallic, has a peak in its resistivity near 40 K, and, although not shown, has zero resistance below about 2 K. The room-temperature resistivity decreases with x up to $x = 0.1$, but increases rapidly at higher x. However, the addition of only 2 mole% Li is enough to destroy the remnants of high-T_c superconductivity and establish VRH conductivity instead. Furthermore, the value of T_0 is insensitive to Li concentration. Table I shows the fitting parameters for the data of Figs. 1 and 2. The T_0's are in the range $0.3-7 \times 10^6$ K and the room-temperature resistivities are in the range $10^{-2}-1$ Ω cm. For $x = 0.5$, the resistivity still follows $T^{-1/4}$, but T_0 is 10^8 K. It is known[11] that this composition is also different in its magnetism, being diamagnetic whereas all the others are paramagnetic.

It is important to emphasize that the VRH behavior is not peculiar to La_2CuO_4 containing Li. The reduced pure ceramic shows the same behavior, at least below 40 K, with about the same T_0 as the crystals from Li flux and Li-containing ceramics, and the crystal grown in CuO also obeys the $T^{-1/4}$ law, albeit with a somewhat smaller T_0. As discussed below, Li is expected, because of its size, to replace Cu and be an acceptor. On the other hand, oxygen vacancies should be donors. We have measured the sign of the thermopower, however, and find that in all samples current is carried by holes, just as it is in the superconductors.[12]

Several of the samples in Figs. 1 and 2 show deviations

TABLE I. Room-temperature resistivity and fitting parameters for those samples characterized by variable-range hopping conductivity. The notations in parentheses indicate the flux used in crystal growth, as discussed in the text.

Sample	ρ (300 K) (Ω cm)	T_0 (10^6 K)	ρ_0 (Ω cm)
$La_2Cu_{0.975}Li_{0.025}O_4$ ceramic	5.2×10^{-2}	2.1	1.6×10^{-4}
$La_2Cu_{0.95}Li_{0.05}O_4$ ceramic	2.6×10^{-2}	1.3	2.5×10^{-4}
$La_2Cu_{0.9}Li_{0.1}O_4$ ceramic	1.7×10^{-2}	1.7	8.0×10^{-5}
$La_2Cu_{0.8}Li_{0.2}O_4$ ceramic	7.1×10^{-2}	3.3	1.8×10^{-4}
$La_2Cu_{0.5}Li_{0.5}O_4$ ceramic	$5.9\times10^{+2}$	97.0	7.5×10^{-6}
La_2CuO_4 reduced ceramic	8.9×10^{-1}	2.6	1.8×10^{-2}
La_2CuO_4 single crystal (Li)	2.7×10^{-2}	2.5	9.8×10^{-5}
La_2CuO_4 single crystal (Li)	1.4×10^{-3}	7.1	5.0×10^{-7}
La_2CuO_4 single crystal (CuO)	4.6	0.3	1.5
La_2CuO_4 single crystal (+$Sr_{0.2}$)	1.1×10^{-1}	2.3	7.4×10^{-4}
La_2CuO_4 single crystal (+$Sr_{0.5}$)	3.4×10^{-2}	0.13	3.3×10^{-3}
La_2CuO_4 single crystal (+Sr_1)	1.4×10^{-1}		
La_2CuO_4 single crystal (+Sr_2)	6.6×10^{-1}		
La_2CuO_4 ceramic	1.4		
La_2CuO_4 oxidized ceramic	5.7×10^{-2}		

from the VRH law at low or high temperature. The resistance at low T is so large and so strongly temperature dependent that the measurements are subject to a variety of systematic errors. This is not the case at the high temperatures, however, so the deviations from the VRH law near room temperature are genuine. For the Li-doped ceramics and the single crystals the deviations can be described as a leveling off of the resistivity when T approaches 300 K or ρ reaches 10^{-1}–10^{-2} Ωcm. The deviation for the reduced ceramic is different, however. Above about 40 K the resistivity has a temperature-independent activation energy, in contrast to the VRH activation energy $\propto T^{3/4}$. The fact that the high-T resistance is activated even though the T_0 is similar to that in the Li-containing crystals (Table I) suggests that the reduced ceramic may be inhomogeneous, containing some regions in which the VRH conductivity dominates and others in which the conductivity is simply activated.

B. Metal-nonmetal transition

Figure 3 illustrates the evolution of the resistivity as the pure ceramic loses oxygen. Plotted in Fig. 3 is the resistivity of (i) a sample annealed in 130 atm of O_2 at 1225 K and cooled slowly, (ii) an as-prepared sample, (iii) the sample of Fig. 1 annealed in a low flow of Ar at 675 K, and (iv) a sample annealed in a rapid flow of Ar to reduce the oxygen partial pressure as far as possible. The thoroughly oxygenated ceramic shows a superconducting transition at 38 K as reported elsewhere;[13] the as-prepared sample shows evidence of superconductivity, but with a very broad transition, reaching zero resistance below about 2 K; the partially reduced sample has a constant activation energy of approximately 30 meV at high T and displays VRH at low T; the thoroughly reduced sample, however, is consistent with simple activated conductivity. The activation energy varies from sample to sample in the range 40–70 meV. Note that the VRH behavior of the partially reduced sample shows up in this $1/T$ plot as a continuously decreasing slope as T is reduced. Measurements for one reduced sample were extended up to 850 K in Ar, but, although a large increase in resistivity occurred at ~650 K, unlike earlier reports,[14] no large activation energy was observed. Measurements on reduced ceramics with controlled oxygen content are underway in order to make this study of the metal-

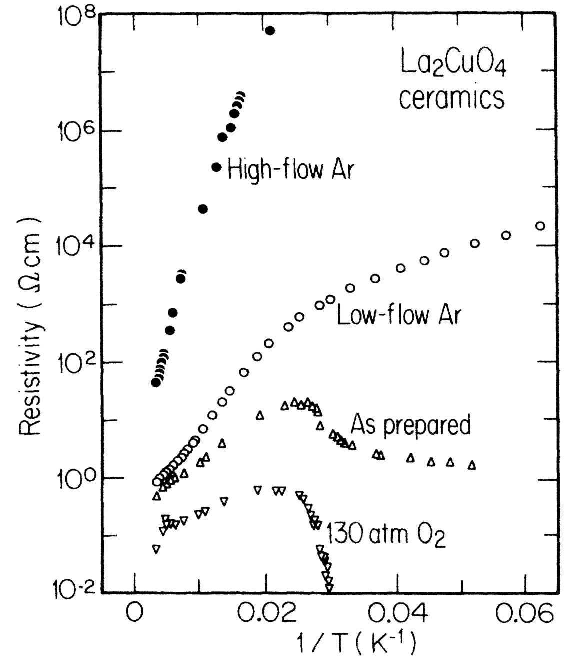

FIG. 3. Resistivity vs T^{-1} for pure La_2CuO_4 ceramics with different oxygen and heat treatments. The absolute oxygen content is unknown.

nonmetal transition quantitative.

No evidence of a large gap has been found in our measurements although a gap of ~2 eV is inferred from optical experiments.[15] The samples are opaque at all photon energies from about 1 meV to about 4 eV. However, even if the Fermi energy were in the gap, the materials might still be opaque because of absorption by impurities or defects. Therefore, we made an exhaustive search for photoconductivity in both single crystals and reduced ceramics in the hope that at low temperatures recombination at such imperfections would become slow enough to allow band-gap photoconductivity to be manifest, as happens in many semiconductors. However, only very small bolometric effects and no photoconductivity were observed at photon energies from 0.3 to 3 eV.

C. Absence of superconductivity in crystals from Li flux

In an attempt to produce superconducting samples, crystals were grown in fluxes containing increasing concentrations of Sr. In Fig. 4 are plotted the resistivities of single crystals grown from fluxes containing $Sr_yLa_2CuO_4$ with y between 0.2 and 2. It is obvious that the addition of Sr increases the conductivity at low concentrations. In fact, the crystal grown with $y=0.5$ has a temperature dependence so weak that the resistivity at 4 K is only 8 Ω cm. On the other hand, we were not successful in producing a truly metallic crystal, for when the Sr content of the flux exceeded 0.5, the conductivity actually decreased again.

From both the lattice constants and the T-O transition temperatures, we know that the amount of Sr incorporated into the crystal is much less than that in the flux. Specifically, by comparison with the T-O transition temperatures in $La_{2-y}Sr_yCuO_4$ ceramics we conclude that in our single crystals $y \lesssim 0.1$. This could be enough to produce superconducting behavior. However, the Li incorporated from the flux undoubtedly inhibits superconductivity. Figure 5 shows the resistivity of a series of ceramics of composition $La_{1.8}Ba_{0.2}Cu_{1-x}Li_xO_4$ with $x=0$, 0.025, and 0.05. The superconducting transition temperature is strongly depressed by small amounts of Li; similar concentrations of Li are present in the single crystals.

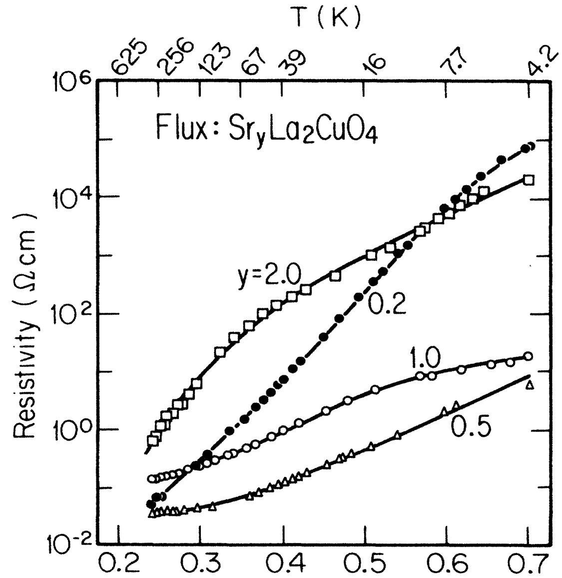

FIG. 4. Resistivity of crystals grown in Sr-containing flux. Note that the least resistive has ρ only ~8 Ω cm at 4 K. However, none of the crystals is truly metallic.

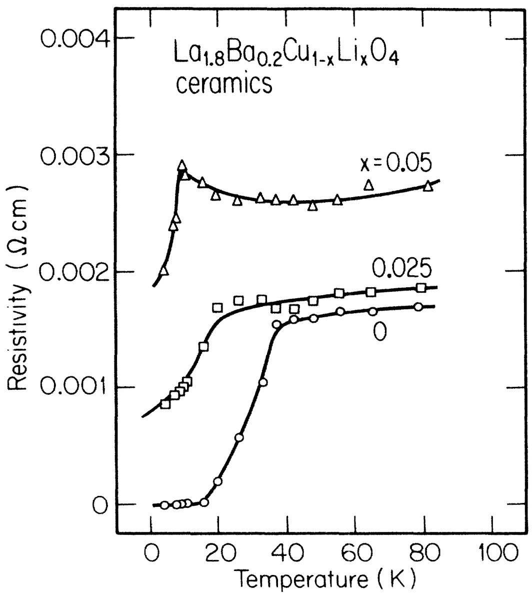

FIG. 5. Suppression of T_c by Li in Ba-containing ceramics.

IV. DISCUSSION AND CONCLUSIONS

In amorphous semiconductors, where VRH has been studied most intensively,[9,16] the $T^{-1/4}$ dependence is overwhelmed at high T by conductivity resulting from activation of charge carriers from the Fermi energy to the conduction or valence band. Because the Fermi level lies in a large gap, this gives a conductivity with large activation energy.

The magnetic properties led us to expect a large gap in La_2CuO_4 as well. Consider the origin of the antiferromagnetism. Although the electronic configuration of Cu^{2+} is d^9, and the appropriate description of the excitations of the ion is in terms of holes, the half-filled $d_{x^2-y^2}$ orbital appears to be well separated in energy from the other d orbitals because of the large tetragonal crystal field. The problem may, therefore, be reduced to that of a single, half-filled orbital on each Cu site, for which the description in terms of holes is equivalent to that in terms of electrons; we choose the latter for simplicity. In a one-electron picture,[17] the extended states near E_F arise from the Cu $d_{x^2-y^2}$ and oxygen p antibonding orbitals, and since there is only one electron per Cu atom, one-electron theory predicts a normal, paramagnetic metal. However, the presence of antiferromagnetism makes it clear that the electron gas in this material is highly correlated, so that one-electron theory is inadequate. A better picture is that of the Mott insulator,[9,18] in which the electrons are not in extended states, but instead are localized, one per Cu^{2+} ion. The on-site Coulomb interaction splits the one-electron band into singly and doubly occupied bands, separated by the correlation energy U. This situation is often approximated by the Hubbard model,[19] and the two bands are, therefore, labeled the lower (singly occupied) and upper (doubly occupied) Hubbard bands. When the lower band is filled, that is, when there is one electron per site, the system is predicted to be an antiferromagnetic insulator with a gap of order U.

Therefore, the clear evidence of antiferromagnetism makes the absence of a large energy gap in our samples very surprising. The Néel state observed in neutron-scattering experiments is now known[5] to result from the three-dimensional ordering of the two-dimensional QSF state which is highly-correlated over large length scales at higher temperatures. Evidence that the ordering is three-dimensional came, in part, from the observation that the peak in the magnetic susceptibility of the pure reduced ceramic is close to the transition temperature[14] rather than well below it, as for previously studied 2D transitions.[20] The reduced ceramic, whose resistivity shows the VRH behavior in Fig. 1, reveals the same susceptibility peak in SQUID magnetometer measurements.[21] The Li-containing ceramics and crystals show no such three-dimensional peak, presumably because the impurities reduce the intralayer and interlayer spin correlations. On the other hand, our Li-containing crystals do show the signature of the QSF state in neutron-scattering experiments. That the conductivity of these samples is limited by hopping means that the electronic states at the Fermi energy are localized by disorder. We conclude, therefore, that the antiferromagnetic ordering occurs in a phase which is nonmetallic, not primarily because of a large energy gap, but because the states at the Fermi energy are localized.

The most straightforward interpretation of our results is that the Fermi energy lies near, but on the localized side of, the mobility edge in the lower Hubbard band. The evidence for this is the following: First, the sign of the charge carrier is positive whether the VRH is induced by Li or by oxygen vacancies. This is not surprising for Li, for when Li^{1+} replaces Cu^{2+} holes are created to preserve charge neutrality. If these are localized on Cu ions, they produce Cu^{3+}, although at low concentrations it is more likely that the holes are extended over several Cu and oxygen ions. In any event, the addition of Li is expected to lower the Fermi level into the singly occupied band just as Sr does. This probably accounts for the fact that addition of small amounts of Li increases the room-temperature conductivity as shown in Fig. 2. It is surprising, however, that such similar VRH behavior is induced by oxygen vacancies. Oxygen vacancies replace sites with charge -2 by sites with charge zero, thereby adding electrons to or reducing the number of holes on the Cu ions.

Second, T_0 is relatively insensitive to composition (see Table I), indicating that the addition of a few percent of oxygen vacancies is inadequate to move the Fermi level out of the band into the gap. Although this pinning of the Fermi energy could, in principle, arise from chemical compensation, between Li impurities and oxygen vacancies, for example, or from collective effects such as solitons, as posited for polyacetylene,[22] the simplest hypothesis is that the single-particle density of states is large enough to pin E_F.

Last, there is no evidence for the large activation energy in the conductivity seen in amorphous semiconductors and impurity-band conduction when E_F is well separated from the mobility edge. The similar value of T_0 for the reduced and Li-containing ceramics is strong evidence that we are not witnessing impurity-band conduction. Thus, it appears that E_F must be situated in a slowly varying density of localized states, and the mobility on the extended side of the mobility edge must be sufficiently low that the hopping current is larger than that arising from thermal activation to the mobility edge. Mott has recently discussed[23] the parameters that enter the prefactor of the latter contribution.

In amorphous semiconductors the $T^{-1/4}$ dependence cannot be followed to very low temperatures because the values of T_0 are so large, typically[16] 10^7–10^8 K, that the resistivity quickly becomes too large to measure as T is reduced. The temperature range over which the $\exp((T_0/T)^{1/4})$ behavior extends in Fig. 1 is very wide, making this one of the best examples of VRH known. The quantity k_BT_0 is the mean energy difference between localized states that are spatially separated by less than one localization length. That is

$$k_BT_0=4\nu_c[g(E_F)\xi^3]^{-1} , \tag{2}$$

where $g(E_F)$ is the density of states at the Fermi energy, ξ is the localization length, and ν_c is a dimensionless constant characterizing the percolation network.[10] For three dimensions it is expected that $\nu_c \cong 4$. The observation that T_0 is smaller in La_2CuO_4 than in amorphous semiconductors reflects a larger localization length or a higher density of states. It is common to use the Pauli susceptibility to determine $g(E_F)$ or arguments based on EPR to estimate ξ, thus separating the contributions of the two quantities to T_0. Because of the QSF state in La_2CuO_4, however, these magnetic measurements cannot be so simply interpreted.

Because we cannot use the magnetism, we appeal to band-structure calculations which indicate[17] that $g(E_F)$ is a few times $10^{21}/\mathrm{cm}^3\,\mathrm{eV}$. If the variation in T_0 comes from differences in $g(E_F)$ the smallest T_0 ($\sim 10^5$ K) corresponds to a value of $g(E_F)$ of this order. One then concludes that ξ is ~ 10 Å and that the different values of T_0 (Table I) arise from different values of $g(E_F)$, the range 3×10^5–7×10^6 K corresponding to the range 10^{19}–$10^{20}/\mathrm{cm}^3\,\mathrm{eV}$. Although our estimate of ξ is rather crude, the localization length can neither be much smaller nor much larger than 10 Å. If it were much smaller, the length would be of the order of the interatomic spacing and the density of states would be unphysically large. A much larger length would require a density of states so low as to be found only in an energy gap. As discussed above, we find no evidence of such a gap.

Objections have been raised[24] over the years to the hypotheses made in the usual theoretical treatment of VRH resistivity. Among these are the presumption that $k_B T$ is much less than the energy of phonons assisting the hopping process and the assumption that only a single phonon is involved in each hop. These objections are probably not relevant to the case of La_2CuO_4, however. At the highest temperature for which we observe the $\exp((T_0/T)^{1/4})$ dependence, the differential activation energy of the resistivity is about 16 meV, approximately the energy of zone-boundary acoustic phonons.[3] Since the energies of optical phonons extend up to ~ 800 meV, there is no reason to believe that a low-temperature form is inappropriate for $T < 100$ K. There is also no direct evidence for or against the strong electron-phonon coupling that might lead to multiphonon processes. However, the unusually strict adherence to the VRH form makes it appear unlikely that such processes are important.

An amusing possibility is that the hopping process is assisted by magnons rather than phonons. The spin excitations in QSF state have such high energies that there would be no serious limitation to the hopping process at 100 K. Experiments are underway to explore this new mechanism for VRH.

The Li ceramics and Li-containing crystals have low room-temperature resistivities, suggesting high carrier densities, but high values of T_0. This suggests that the addition of Li, while increasing the density of holes, creates sufficient disorder to cause a broad tail of localized states on the band edge which accommodates all the excess holes leaving E_F in a region of localized states. The efficacy of Li in creating disorder is probably the reason why it so effectively suppresses superconductivity. Oxygen vacancies, the most likely source of disorder in the reduced ceramic and the crystal grown in CuO, move the Fermi energy closer to the band edge by reducing the hole density. This may explain the low conductivity of the CuO-grown crystal at high T. Thus, even if vacancies did not create much disorder, they would move E_F into the region of states localized by other sources of disorder. It is very likely, however, that oxygen vacancies and Li, which replaces Cu, are both very effective sources of the localizing potential, since they directly disorder the CuO layers where the valence states are located. This explains why the effect of Li is so different from that of Sr, which replaces La instead of Cu.

Oxygen vacancies and Li suppress superconductivity in strikingly different ways. As seen in Fig. 3 the ceramic annealed in 130 atm of O_2 has zero resistance below about 40 K. For the as-prepared ceramic the resistance begins to decrease at about 40 K, but decreases gradually, reaching zero only at ~ 2 K. By contrast, Fig. 5 shows that for the Li-doped samples, the transition remains sharp for all concentrations of Li, but the transition temperature is depressed.

There are two ways of suppressing superconductivity. If the order parameter is written as

$$\Psi = \Delta e^{-i\phi} , \tag{3}$$

then superconductivity may be destroyed by reducing Δ or by destroying phase coherence. In granular superconductors the two effects can be separated.[25] Disorder within the grain decreases the effective coupling strength, primarily by increasing the Coulomb interaction, resulting in smaller Δ. This results in lower T_c, but the transition remains sharp. On the other hand, reducing the coupling between grains by increasing the width or degree of disorder of the grain boundaries destroys phase coherence. The latter results in a broadening of the transition on the low-temperature side, but the transition begins at the value of T_c characteristic of the superconducting grains.

The data of Fig. 3, thus, suggest that loss of oxygen suppresses superconductivity in La_2CuO_4 by destroying phase coherence. This implies that even in the as-prepared sample there are grains that become superconducting at ~ 40 K. On the other hand, the data of Fig. 5 indicate that the addition of Li reduces the magnitude of the order parameter, so no superconductivity remains at all once more than a few percent of Li is added.

Variable-range hopping gives the dependence $\exp((T_0/T)^{1/(d+1)})$ in d dimensions, so the $T^{-1/4}$ dependence is consistent with the isotropic conductivity in the crystals (Fig. 1). However, it is quite surprising to find no anisotropy in the conductivity of crystals which have almost purely two-dimensional magnetism.[5] This may be understood by remembering that VRH is actually a percolation process in which the resistivity is determined by the least resistive percolation path through the sample. The hopping would be two dimensional only if such a path could be completed within a single layer before hopping to adjacent layers completed a three-dimensional path. This is unlikely because of the higher percolation threshold concentration in two rather than three dimensions (0.24 for the nearest-neighbor bcc lattice compared with 0.59 for the nearest-neighbor square planar lattice).

An immediate consequence of this work was already mentioned in our study of the T-O transition.[3] Since the states at E_F are localized, theories[19] that begin with the hypothesis that the structural instability results from Fermi-surface effects appear untenable. There is obviously no evidence for the charge-density wave proposed[26] to account for the insulating state.

In summary, we find that the state of La_2CuO_4, in which the T-O and antiferromagnetic transitions as well as the quantum spin fluid have been observed, is nonmetallic because the electronic states at the Fermi energy are localized. Despite a thorough search, we find no evidence of a large energy gap. The results suggest that the Fermi energy lies not in such a gap, but, instead, near the top of the singly occupied (lower Hubbard) band for the nonmetal as well as the superconductor.

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