PHYSICAL REVIEW B VOLUME 47, NUMBER 9 1 MARCH 1993-I

Copper oxide superconductors: A distinguishable thermodynamic state

J. B. Goodenough, J.-S. Zhou, and J. Chan
Center for Materials Science and Engineering, University of Texas at Austin, Austin, Texas 78712-1084

(Received 13 May 1992; revised manuscript received 29 September 1992)

The temperature dependence of the resistivity and Seebeck coefficient for the two p-type systems $La_2CuO_{4+\delta}$, $0 \le \delta \le 0.09$, and $La_{2-x}Sr_xCuO_4$, $0 \le x \le 0.3$, are reported and interpreted in the context of overall phase diagrams. Above room temperature, the $La_2CuO_{4+\delta}$ system tends to lose oxygen at 1 atm O_2; superconductive samples exhibit a first-order loss of oxygen above 500 K to revert to the antiferromagnetic phase. Below a transition temperature $T_s \approx 300$ K, compositions with $0 < \delta < 0.05$ undergo phase segregation to an antiferromagnetic and a superconductive phase; the superconductive phase appears to undergo a further dynamic segregation into hole-rich and hole-poor domains in the interval $T_c < T < T_\rho \approx 100$ K. In the system $La_{2-x}Sr_xCuO_4$, the holes move diffusively, with a $\Delta H_m = 0$, above $T_l \approx 300$ K for the compositions $0 < x \le 0.21$; the system undergoes a transition from a p-type two-dimensional conductor to an n-type three-dimensional conductor in the interval $0.22 \le x < 0.35$. Compositions with $0 < x \le 0.12$ are metastable in the range $T_c < T < T_l$ where the holes continue to move diffusively, but charge fluctuations appear in the range $T_c < T < T_\rho \le 150$ K. Compositions with $0.15 \le x \le 0.2$ appear to undergo a transition from a polaronic gas to a polaronic (Luttinger) liquid on cooling through T_l; superconductive pairs are condensed from the homogeneous polaronic-liquid normal state at T_c. The origin of the unusual electron-lattice interactions in the normal state of the superconductive compositions is attributed to a coexistence of ionic and covalent bonding at a transition from more ionic to covalent Cu:$3d_{x^2-y^2}$-O:$2p_\sigma$ bonding in the CuO_2 sheets; through the transition the orbital hybridization and Hubbard U parameter vary sensitively with both the Cu-O bond length and the formal local oxidation state at a Cu atom.

I. INTRODUCTION

High-T_c superconductivity in the copper oxides is associated with mixed-valent CuO_2 sheets that are either oxidized or reduced from the $(CuO_2)^{2-}$ oxidation state of an antiferromagnetic, semiconductor parent compound and have all their Cu atoms in the same oxygen coordination. Moreover, a full Meissner fraction (the volume used in the calculation is limited to the CuO_2 planes) and a saturation value of T_c appear to be associated with a narrow range of charge-carrier concentrations per Cu atom: $0.12 < p \le 0.20$ in the p-type $La_{2-x}Sr_xCuO_4$ system, for example.

In this paper we argue that the electrons (or holes) near the Fermi energy in the CuO_2 sheets of the superconductor compositions are thermodynamically distinguishable not only from those in the parent compound, but also from those in the more deeply oxidized or reduced compositions that are conventional metals. In order to demonstrate this proposition, we compare the properties and phase diagrams of two p-type systems, $La_2CuO_{4+\delta}$ and $La_{2-x}Sr_xCuO_4$, which are related to one another by a common parent, La_2CuO_4, having the structure of Fig. 1. In each system, oxidation of the CuO_2 sheets is accomplished without changing the oxygen coordination at a Cu atom. The data for these two systems indicate the formation of intermediate-size polarons at temperatures $T > T_l$ where, in the system $La_{2-x}Sr_xCuO_4$, there is a complete range of solid solutions from a parent antiferromagnetic phase ($x = 0$) to a conventional metal ($x > 0.27$). Below $T_l \simeq 300$ K, the polarons appear to become coupled: for hole concentrations p per Cu atom in the range $0 < p < 0.12$, a phase segregation into the antiferromagnetic and superconductive phases proceeds by a classic ion diffusion and/or a dynamic, cooperative displacement of atoms that modulate the Cu-O bond lengths; for the superconductive $0.12 < p \le 0.20$ compositions, there is no phase segregation, but the polarons and their motions appear to become strongly coupled to one another in the normal state. This unique normal state we call a "polaron liquid"; we distinguish it from the "polaron gas" at temperatures $T > T_l$. At higher values of p the potential wells of the "dressed" charge carriers overlap sufficiently to suppress the strength of the electron-phonon interactions, and conventional metallic behavior is restored. The transition from a superconductor to a conventional metal with increasing charge-carrier density appears to be smooth above room temperature; preliminary measurements indicate it may not be smooth at lower temperatures.

We argue further that stabilization of high-T_c superconductivity is found not only where strong electron-electron interactions characterize the parent phase, but also where, in the mixed-valent compositions, there is an exceptional sensitivity of the on-site Coulomb energy U (the Hubbard U) to the lattice Madelung energy as a result of a crossover from a crystal field to a covalent description of the states associated with the upper Hubbard band. Moreover, the strength of the local Madelung energy, which also modulates the local charge-carrier concentration (p or n) in a mixed-valent system, varies

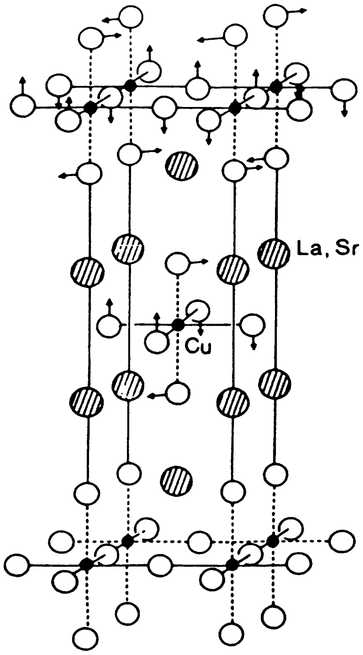


FIG. 1. The tetragonal structure of high-temperature ($T > T_t$)La_2CuO_4. Arrows indicate directions of cooperative rotations of CuO_6 octahedra in the orthorhombic phase $T < T_t$.

with the local mean Cu-O bond length; the result is a strong electron (hole)-lattice interaction. At lower temperatures ($T < T_c$), the electron-lattice interactions may be strong enough to induce the formation of Cooper pairs within "bags" provided the change in the local effective U is strong enough for the electron-phonon interaction to overcome the electrostatic repulsion between the electrons (holes) of a pair. We have referred to this mechanism as a "correlation-bag" model of high-T_c superconductivity.[1] It is to be distinguished from a large bipolaron model[2] on the one hand and a "spin-bag" model[3] on the other.

Finally, we cite experimental data[4] showing that the Madelung energy is significantly smaller in the n-type superconductors and decreases with increasing n so as to allow, in these systems also, the essential crossover from more ionic to covalent $Cu{:}3d_{x^2-y^2}\text{-}O{:}2p_\sigma$ bonding for the states in the upper Hubbard band.

A. The system $La_2CuO_{4+\delta}$

The prototype parent compound La_2CuO_4 has the tetragonal K_2NiF_4 structure of Fig. 1 above a temperature T_t; at lower temperatures it becomes orthorhombic due to a cooperative rotation of the CuO_6 octahedra (indicated by arrows in Fig. 1) that buckles the Cu-O-Cu bond angle from 180°. The distortion below T_t relieves a compressive stress on the CuO_2 sheets that is caused by a mismatch, which increases with decreasing temperature, of the equilibrium La-O bond length in the La_2O_2 layers and the Cu-O bond lengths of the CuO_2 sheets. Oxidation of the $(CuO)^{2-}$ sheets also relieves the compressive stress by shortening the Cu-O bond length, and the parent compound can be made a p-type superconductor [$T_c = 40$ K (Ref. 5)] by oxidizing the CuO_2 sheets without changing the oxygen coordination at any Cu atom. One way to do this is by the insertion of excess oxygen between the LaO planes of the LaO-LaO rocksalt layers.[6]

Insertion of excess oxygen has been achieved by annealing under a high oxygen partial pressure or by low-temperature electrochemistry. Grenier *et al.*[7] have developed electrochemical oxidation as a room-temperature synthetic technique allowing a controlled variation of the excess oxygen content of $La_2CuO_{4+\delta}$ over the compositional range $0 \leq \delta \leq 0.09$. X-ray powder diffraction at room temperature shows a transition from an O-orthorhombic to an O_M-orthorhombic phase near $\delta \simeq 0.05$; the distortion to orthorhombic symmetry decreases with increasing δ in the O-orthorhombic phase, becoming nearly tetragonal at room temperature for $\delta \simeq 0.05$, but increases with δ in the O_M phase. A thermogravimetric analysis and differential scanning calorimetry on a $\delta \approx 0.05$ sample prepared under high oxygen pressure[8] showed a gradual loss of oxygen at atmospheric pressure on heating above room temperature with a first-order loss of oxygen near 500 K on reverting to the parent phase. A discontinuous expansion of the Cu-O bond length occurred across the transition on passing from the superconductor to the antiferromagnetic phase.

Lagueyte[9] has reported transport and magnetic measurements as a function of temperature $T < 300$ K for several compositions of this system; representative data from the O and O_M phases are shown in Fig. 2. Interpretation of the data to obtain the phase diagram of Fig. 3 is discussed elsewhere in detail.[10] Several striking features are reviewed here.

1. Phase segregation

Jorgensen *et al.*[11] noted a phase segregation below 320 K in a $\delta \approx 0.03$ sample. Ryder *et al.*[12] have demonstrated indirectly that the interstitial (excess) oxygen remain

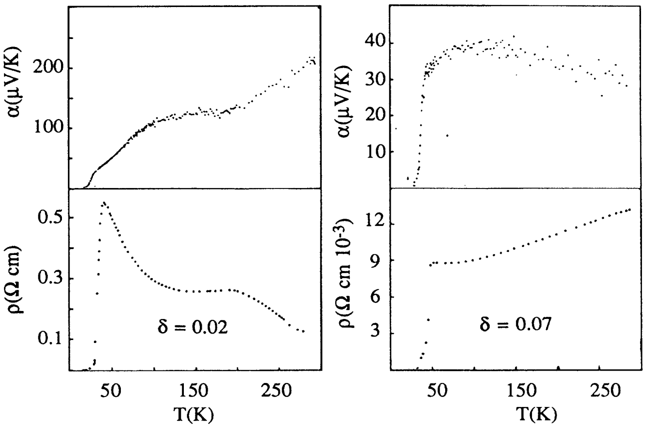


FIG. 2. Temperature variation of the Seebeck coefficient α and resistivity ρ for $La_2CuO_{4+\delta}$ with $\delta = 0.02$ and $\delta = 0.07$, after Ref. 10.

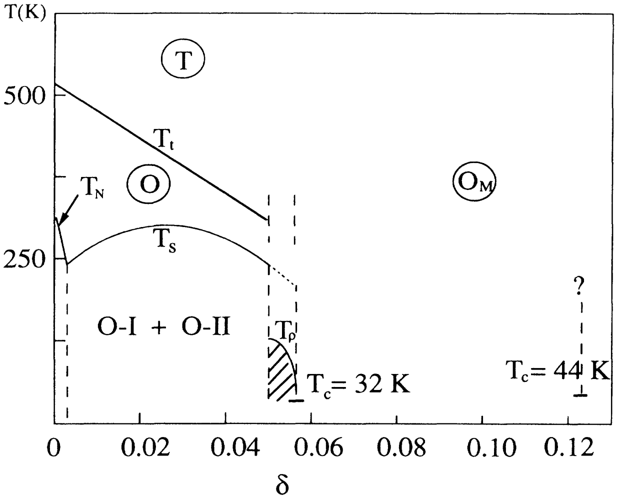


FIG. 3. Phase diagram for $La_2CuO_{4+\delta}$.

mobile in this system down to 200 K. Phase segregation within the O-phase field is to a composition O-I near that of the parent compound ($\delta \approx 0$) on one side[13] and to a superconductive composition O-II near $\delta \approx 0.05$ on the other. As can be seen for the $\delta = 0.02$ sample of Fig. 2, the resistivity increases and the Seebeck coefficient decreases with decreasing temperature throughout the interval $200 < T \leq T_s$, where T_s is the onset temperature for the spinodal decomposition. The degree of phase segregation apparently continues to develop throughout this temperature range, but is prevented from going to completion by a freezing out of the oxygen mobility below 200 K.

The temperature variations of α and ρ in the range $200 < T < T_s$ are taken to be a signature of a developing phase segregation; therefore, similar temperature variations of α and ρ below a $T_\rho \approx 100$ K are taken to represent the manifestation of a residual metastability in the oxygen-rich phase. This low-temperature feature was common to all samples $0.01 \leq \delta \leq 0.04$, but it did not appear in any samples in the range $0.06 \leq \delta \leq 0.09$. Therefore, in the phase diagram of Fig. 3 we represent a further segregation within the O-II phase into hole-rich and hole-poor domains below T_ρ in the range $0.04 \leq \delta < 0.06$. At temperatures $T < T_\rho$, no ions are mobile and any further segregation into hole-rich and hole-poor regions within the oxygen-rich phase can only occur via cooperative atomic displacements that create domains of different mean Cu-O bond length. These displacements appear to be dynamic, and we suggest that the temperature variations of α and ρ below T_ρ reflect charge fluctuations that develop progressively with decreasing temperature. Further support for this suggestion comes from the system $La_{2-x}Sr_xCuO_4$, which we discuss in detail below.

2. *The phases O and O_M*

The phase segregation that occurs within the O-orthorhombic phase field is not to be confused with the change to an O_M distortion at larger δ. The orthorhombic-tetragonal transition temperature T_t decreases with increasing $\delta \leq 0.05$, where the interstitial oxygen remain randomly distributed as O^{2-} ions among the interstitial sites within a rocksalt layer since both the introduction of interstitial oxygen and oxidation of the CuO_2 sheets relieves the compressive stress on the CuO_2 sheets. However, for $\delta > 0.05$ there appears to be either an ordering of the excess oxygen among the interstitial sites or an ordering of O-O bonding with $(\delta - 0.06)$ neutral oxygen within the rocksalt layers; increasing occupancy of the ordered array of interstitial sites causes the orthorhombic distortion to increase with δ. This phase change is to be distinguished from the spinodal disproportion into oxygen-rich O-II and oxygen-poor O-I phases.

3. *The superconductor compositions*

It is significant that the spinodal disproportion does not separate the parent phase from a conventional-metal phase, but from a narrow range of superconductor compositions. This fact has suggested to us[14] that the electronic state in the superconductor compositions is thermodynamically distinguishable not only from that of the antiferromagnetic parent phase, but also from that of the conventional-metal phase of the more heavily doped compositions.

The temperature variations of ρ and T for the $\delta = 0.07$ sample, Fig. 2, are completely different from those of the $\delta = 0.02$ sample. Whereas the $\delta = 0.02$ sample is representative of all the compositions $0.01 \leq \delta \leq 0.04$, the ρ vs T and α vs T of the $\delta = 0.07$ sample are representative of all compositions $0.06 \leq \delta \leq 0.09$. A $\rho \sim T$ from 90 K to room temperature is typical of all the copper oxide superconductors having $0.06 \leq \delta \leq 0.09$. Moreover, above 90 K the Seebeck data for $\delta = 0.07$ are characteristic of an unusually strong mass enhancement.[15] No phase segregation, static or dynamic, is evident. Nevertheless a peculiar step occurs in the resistivity drop associated with T_c. The step remains a step over the entire compositional range $0.04 \leq \delta \leq 0.09$; at no composition does the higher-temperature superconductive phase percolate through the crystal. The ac susceptibility data show that only a small fraction of the sample becomes diamagnetic in the range $30 < T < 44$ K, the diamagnetism is field independent, and there are no magnetic losses in this temperature interval. This ac susceptibility behavior is similar to what is observed for all $T < T_c$ in the $\delta = 0.04$ sample where we have argued that the superconductivity is associated with charge fluctuations within the oxygen-rich phase. Finally, the transport data for all compositions $0.06 \leq \delta \leq 0.09$ were similar to those for $\delta = 0.07$ shown in Fig. 2, which indicates that the hole concentration in the CuO_2 sheets is not varying with δ for $\delta > 0.06$. It appears that the oxygen atoms in excess of $\delta \simeq 0.06$ enter the sample as neutral oxygen, probably forming O-O bonds as in a peroxide $(O_2)^{2-}$ ion. Therefore, our measurements could not distinguish whether the resistivity step at T_c signals the presence of a second, higher-temperature superconductive phase or the onset of pair fluctuations.

The dc magnetic susceptibility shows the onset of a bulk diamagnetic Meissner effect at 44 K for all samples $0.06 \leq \delta \leq 0.09$, whereas the $\delta = 0.04$ sample shows the onset of diamagnetism at $T = 30$ K with a significantly smaller Meissner fraction.

The assertions made in our interpretation of the data for the system $La_2CuO_{4+\delta}$ take on more credence when compared to similar data for the system $La_{2-x}Sr_xCuO_4$ in which there are no mobile ions and the stoichiometry remains stable to 900 K.

B. The system $La_{2-x}Sr_xCuO_4$

1. *Experimental*

All samples were prepared from an intimate mixture of La_2O_3, CuO, and $SrCO_3$ by standard ceramic techniques. Preheated samples were fired at 1050 °C and furnace cooled in air with several regrinding and refiring schedules. X-ray powder diffraction showed single-phase material for all compositions $0 \leq x \leq 0.3$. Samples with $x = 0.00$ and $x = 0.01$ were slightly oxygen rich. The $x = 0.30$ sample appears to be a little oxygen deficient. Figure 4 shows typical resistance R vs temperature T curves obtained with a four-probe method below T_c for several values of x; our results are consistent with those reported by Takagi *et al.*[16] The linear dependence of R vs T continues to 800 K.

The Seebeck coefficients α vs T given in Fig. 4 were obtained from the definition

$$\alpha = \lim_{\Delta T \to 0} \frac{\Delta V}{\Delta T} , \qquad (1)$$

where ΔV is the potential generated across the sample by a temperature gradient ΔT. Measurements were made with a home-built apparatus. The temperature gradient across the sample was generated in two separate copper blocks under precise temperature control and making good thermal contact with the sample surfaces. A fixed ΔT and stable ΔV at thermal equilibrium were taken for all temperatures. We plot α^2 vs T to demonstrate the relation $\alpha^2 \sim T$ in the range $T_c < T < T_\rho$ for all compositions $0.02 \leq x \leq 0.065$; the $\alpha^2 \sim T$ relation holds for a shorter temperature interval below T_ρ in the $x = 0.075$ and 0.10 samples. The α^2 vs T curves for $x \geq 0.15$ have a totally different character; they correspond to the curves for $0.06 \leq \delta \leq 0.09$ in the $La_2CuO_{4+\delta}$ system.

Comparison of the α^2 vs T and R vs T curves for each sample in the compositional range $0.02 \leq x \leq 0.10$ shows a temperature-independent α at temperatures $T > T_F$; extension of the temperature range of measurement to 800 K shows that α remains essentially temperature independent to highest temperatures. The sample resistance varies linearly with the temperature, $R \sim T$, from T_ρ to highest temperatures, without any anomaly at T_F; below T_ρ the resistance R deviates from the $R \sim T$ relationship, increasing with decreasing R at lower temperatures. The compositions with $0.02 \leq x \leq 0.045$ show an R increasing continuously with decreasing temperature below T_ρ whereas those with $0.055 \leq x \leq 0.10$ exhibit a superconductive transition T_c that increases with x. Compositions with $0.15 \leq x \leq 0.30$, on the other hand, exhibit R vs T curves approaching $R \sim T$ for all temperatures $T > 40$ K. The step in the R vs T curves near 40 K for $0.2 \leq x \leq 0.30$ samples remains even though T_c decreases with increasing x, vanishing for $x > 0.29$.

A plot of α vs T for $x = 0.15$ is shown in Fig. 5. Above a temperature $T_l \approx 300$ K, the Seebeck coefficient changes its temperature dependence, becoming nearly temperature independent; the same behavior is found for $x = 0.20$. For $x = 0.25$, the value of α becomes too small above 300 K to be measured accurately with our setup because it becomes comparable to the thermopotential from the copper blocks.

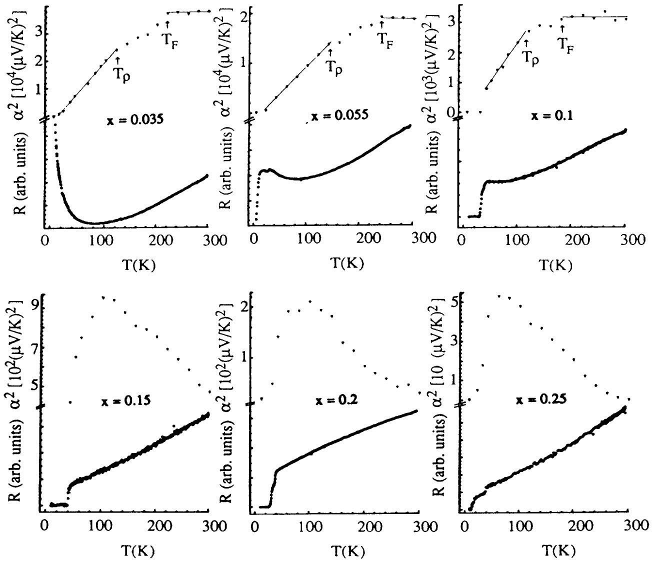


FIG. 4. Temperature variation of the square of the Seebeck coefficient α and the resistance R for different values of x in $La_{2-x}Sr_xCuO_4$. (The lines in figure are a guide to the eye.)

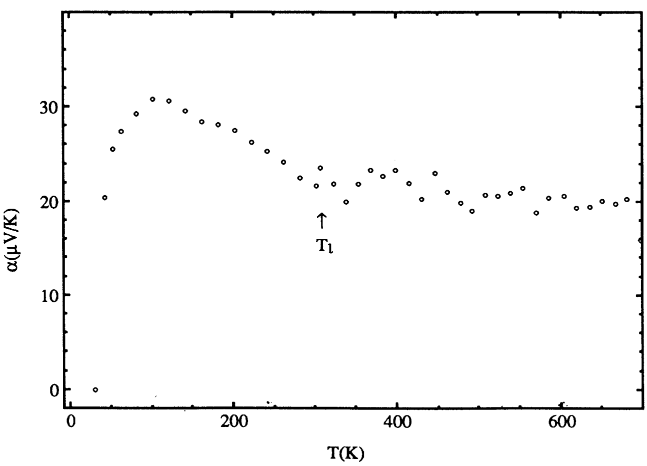


FIG. 5. Temperature dependence of the Seebeck coefficient for $La_{1.85}Sr_{0.15}CuO_4$ showing a transition at $T_l \approx 300$ K.

2. *Interpretation*

We summarize the data for the $La_{2-x}Sr_xCuO_4$ system in the phase diagram of Fig. 6. The rapid drop with x in the antiferromagnetic ordering temperature T_N is now well documented,[17] but the earlier interpretation of a spin-glass region at low temperatures in the compositional range $0.01<x<0.05$ has been questioned;[18] it has been suggested that the magnetic ordering is probably associated with a segregation of the antiferromagnetic phase. Cho *et al.*[8] have argued convincingly for the existence of quasistatic fluctuations of mesoscopic antiferromagnetic domains in the range $0.02 \le x \le 0.08$. This latter suggestion is consistent with our deduction of the existence of charge fluctuations below T_ρ (Ref. 19). The temperature $T_{\max}$ is the temperature at which the paramagnetic susceptibility has its maximum value. A $T_{\max} > T_N$ below which short-range antiferromagnetic spin fluctuations are found is typical of two-dimensional antiferromagnetic systems. Below $T_{\max}$ we can expect to find antiferromagnetic spin fluctuations. We take the $T_{\max}$ vs x curve from the literature.[20] The decrease in the orthorhombic-tetragonal transition temperature T_t is taken from the same source, but we include the more recent results of Takagi *et al.*[21] on the crossover of T_t and T_c at $x=0.21$, which still cannot rule out the possibility that superconductivity extends into the tetragonal phase. The dip in T_c near $x=1/8$ has been attributed to a mode softening at this composition that actually suppresses T_c in the systems $La_{2-x}Ba_xCuO_4$ where a low-temperature tetragonal phase is stabilized.[22] Koike *et al.*[23] have argued that this low-temperature transition is electronically driven and is not the result of a short-range ordering of La^{3+} and Ba^{2+} ions in the rocksalt layers. Nakamura and Uchida[23] provide a more convincing demonstration of the uniqueness of the hole concentration $p=1/8$.

The remaining transition temperatures and compositions marked in Fig. 6 come from this study. First, we note that below T_l there is also a transition with increasing x at $x=1/8$ in the temperature dependence of α; in the compositional range $0 \le x \le 0.10$, α is temperature independent in the interval $T_F < T < 800$ K whereas it is temperature dependent in the interval $T_c < T < T_l$ in the range $0.15 \le x \le 0.25$. Therefore we mark this transition on crossing $x=0.12$ with a hatched vertical line. We note further that the transitions T_F and T_ρ are clearly defined in the range $x \le 0.10$, but not in the range $x \ge 0.15$. The transition at T_l, which is marked by a hatched horizontal line, is not so clearly defined. It represents a measurable change in the character of the charge carriers in the range $0.15 \le x \le 0.20$; we discuss the nature of this transition below. We extend T_l across the range $0 \le x \le 0.10$ because of the observation of spinodal phase segregation in the $La_2CuO_{4+\delta}$ system in this range of oxidation of the CuO_2 sheets. In the $La_{2-x}Sr_xCuO_4$ system we believe it separates temperature ranges of stability and metastability in the interval $0.02 \le x \le 0.10$. In the absence of any mobile ions below T_l, the metastability can only express itself as charge fluctuations below a T_ρ. In both the $La_2CuO_{4+\delta}$ and $La_{2-x}Sr_xCuO_4$ systems, the signature from ρ vs T and α vs T data that we interpreted to indicate charge fluctuations is confined to the oxidation state range $0.01<p<0.12$ where the concentration of holes per Cu atom is $p=x$ or 2δ. (For $x>0.06$ in $La_2CuO_{4+\delta}$ a constant $p \approx 0.12$ is found, as noted above.) The vertical hatched line at $0.20<x<0.25$ represents a more subtle change in the character of the electrons. At low temperatures it marks the boundary between superconductor and unusual-metal compositions; at high temperatures it is marked only by a change in slope of the R vs T curves (Fig. 7). We believe that at higher temperatures a smooth transition occurs beyond this compositional domain from a thermodynamically distinguishable superconductor phase in which the holes, though itinerant, are "dressed" toward a conventional-metal phase in which the electrons may be described as a Fermi liquid. The optical data of Uchida *et al.*[24] provide additional evidence for a transition from a distinguishable normal-state phase at room temperature to almost a Fermi liquid in the interval $0.20<x<0.25$; they also report a change from two- to three-dimensional conductivity in this same interval.

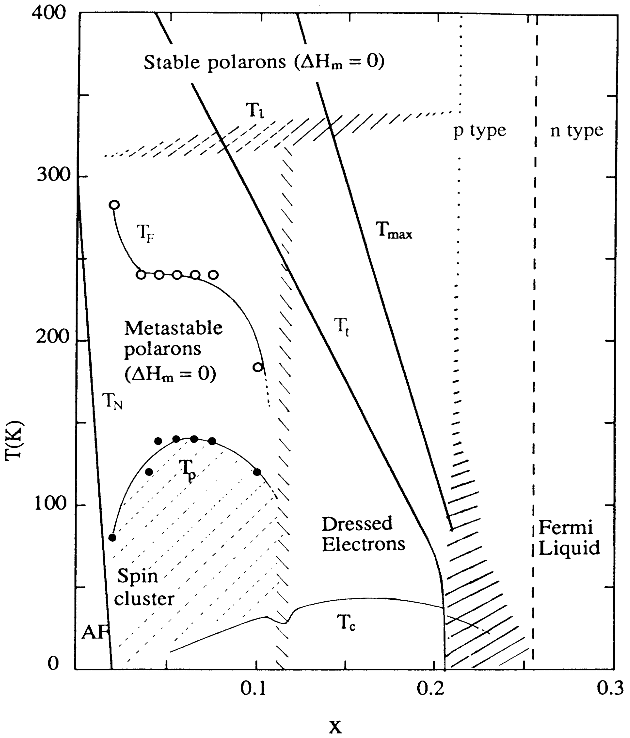


FIG. 6. Phase diagram for $La_{2-x}Sr_xCuO_4$.

The Seebeck coefficient for itinerant electrons is described by the Mott formula

$$\alpha \approx \left[\frac{\pi^2 k^2 y}{3eE_F}\right] T , \qquad (2)$$

which gives a linear temperature dependence for a constant y. In an itinerant electron system with strong electron-phonon interactions, the α of Eq. (2) is mass enhanced by an electron-phonon coupling parameter $\lambda(T)$:

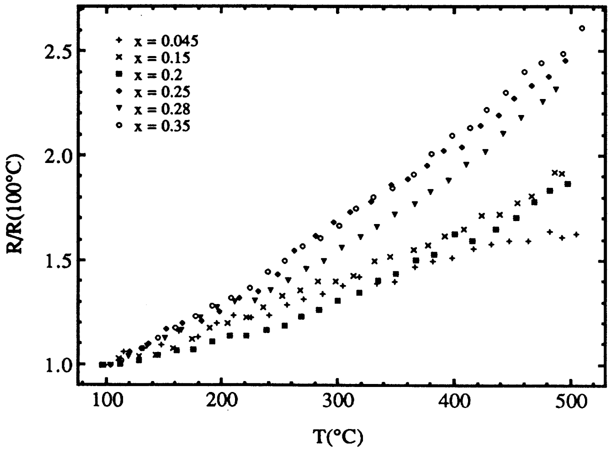


FIG. 7. Normalized resistance vs temperature for different values of x in $La_{2-x}Sr_xCuO_4$.

$$\alpha_m = \alpha[1+\lambda(T)] , \tag{3}$$

where λ increases with decreasing temperature to a higher power.[15] On the other hand, polaronic motion in a narrow-band, mixed-valent oxide contains a negligibly small transport contribution; the dominating configuration term is given by[25]

$$\alpha = -\frac{k}{e}\ln\left[\beta\frac{1-p}{p}\right] , \tag{4}$$

where $\beta=2$ is a spin-degeneracy factor and $p = x$ is the hole concentration per Cu atom in the CuO_2 sheets. The temperature-independent α observed in the compositional range $0 < x \leq 0.10$ for $T > T_F$ is typical of polaronic hopping. However, small polaron holes would be expected to have an activated mobility

$$\mu_p = \frac{eD_0}{kT}\exp\left[\frac{-\Delta G_m}{kT}\right] \tag{5}$$

arising from a motional enthalpy $\Delta H_m > 0$ in the motional free-energy $\Delta G_m = \Delta H_m - T\Delta S_m$. Except at very low values of p, $R \sim T$ in this temperature interval indicates that the holes in the $La_{2-x}Sr_xCuO_4$ system have a $\Delta H_m = 0$; the mobile holes are not collapsed to a single Cu site by a local relaxation of the nearest-neighbor O^{2-} ions. Nevertheless, the temperature-independent α indicates that the holes are hopping in a diffusional motion, so we conclude that the holes are "dressed" in a local deformation, but remain extended, as intermediate-size polarons, over the neighboring oxygen atoms to such an extent that they are able to move via a phonon-assisted hopping with $\Delta H_m = 0$; large polaron motions are on the time scale of the cooperative local lattice fluctuations and are not thermally activated.[26] From this perspective, it is interesting to note that the application of Eq. (4) in the compositional range $0 < x \leq 0.10$ gives too large a value of α; for $x = 0.02$, the measured α is only about two-thirds of the theoretical α, and the discrepancy increases with x. However, for an extended polaron, it is not proper to take N in the fraction $(N-c)/c = (1-p)/p$ to be the total number of Cu atoms since the hole occupies more than one site. We must reduce N to some N^* and replace p in Eq. (4) by $p^* = P/N^* > p$, where $P = Nx$ is the number of holes per N Cu atoms. Use of p^* in Eq. (4) gives $N \simeq 4.5N^*$ for $x = 0.02$, which implies that the holes are extended over four to five Cu atoms. As x increases, the interactions between the polarons increase; in the interval $0.12 \leq x \leq 0.21$, a coupling of the polarons below T_l to form a polaron (Luttinger) liquid with an electronic **k** coupled to a lattice **q** vector would introduce a Fermi surface and a giant mass enhancement.

The spin-degeneracy parameter β normally decreases from 2 to 1 at a long-range magnetic ordering temperature. However, within a CuO_2 sheet the Cu-O-Cu interactions are essentially two dimensional, so short-range antiferromagnetic spin fluctuations are present below $T_{\max}$; they have a fluctuation time τ_F. Where the time τ_h for a hole to hop from one Cu atom to the next contains no activation energy ($\Delta H_m = 0$), $\tau_h \sim \mu_p^{-1}$ decreases with decreasing temperature, and it is possible to have a critical temperature T_F below which a $\tau_F > \tau_h$ changes β from 2 toward 1 as the hopping electrons see locally a magnetically ordered array. The drop in α associated with such a spin-freedom quenching has a maximum value of 60 μV/K. Since the observed drop in α in the interval $T_\rho < T < T_F$ is $\Delta\alpha < 60$ μV/K, we interpret T_F to be the temperature where $\tau_F = \tau_h$; the transition occurring below T_ρ commences before the spin freedom is completely quenched.

In the $La_2CuO_{4+\delta}$ system, we interpreted the decrease in α with decreasing T below T_ρ to be due to a progressive development of charge fluctuations with decreasing temperature.[19] We made this hypothesis on the basis of an α vs T and ρ vs T variation in the interval $T_c < T < T_\rho$ that was similar to the variations induced by a static, classic spinodal phase segregation in the interval $200 < T \leq T_s$. Since the magnitude of α is determined by the hole-rich (oxygen-rich) phase produced by the phase segregation, it follows from Eq. (10) that the progressive segregation of a phase more rich in holes would decrease α and progressive restriction of the conduction paths to the hole-rich domain would increase ρ. In the $La_{2-x}Sr_xCuO_4$ system, there are no mobile ions by which the system can express its metastability below T_l; therefore, the phase can only express its metastability through the onset of cooperative, dynamic atomic displacements that give rise to charge fluctuations below T_ρ. As in the spinodal decomposition, charge fluctuations separate regions rich in holes from those poor in holes; the existence of dynamic fluctuations would not alter the fact that they would have a similar influence on the α vs T and ρ vs T behavior as a static spinodal segregation that develops progressively with decreasing temperature.

In the absence of any evidence for static atomic displacements from x-ray or neutron diffraction, we assume the locally cooperative atomic displacements are dynamic, giving rise to charge fluctuations. Such charge fluctuations would be expected to have a characteristic frequency in the range $10 < \nu_c < 100$ GHz, which corresponds to a period for the cooperative displacements of about 10^{-9} s. Such a period is long compared to the life of a superconductive Cooper pair, so superconductivity can, in principle, occur within a charge fluctuation. Indirect evidence for dynamic charge fluctuations below about 120 K comes from ac measurements to 94 GHz on a nominal La_2CuO_4 single crystal that appears to contain some excess oxygen.[27] A change of slope in the dc resistivity near 200 K is similar to that found for the $\delta \leq 0.02$ sample shown in Fig. 2. The ac measurements[27] show a transition at $T_\rho \approx 120$ K in the temperature variations of both the dielectric constant and the resistivity. Below T_ρ, there is a crossover of the ac resistivities at 60 and 94 GHz that suggests a charge-fluctuation resonance near 60 GHz.

In the compositional range $0.15 \leq x \leq 0.2$, T_c is close to its saturation value and there is no clear evidence of a charge-fluctuation temperature interval $T_c < T < T_\rho$. As in the $La_2CuO_{4+\delta}$ system, the superconductive state that condenses from a homogeneous normal state can be distinguished from the one that condenses from a charge-fluctuation state. In both systems the charge-fluctuation phenomenon is confined to the hole-concentration range $0 < p < 0.12$ and, in the range $0.15 \leq p \leq 0.20$, the α vs T dependence from the maximum in α to room temperature is characteristic of an unusually strong mass enhancement [Eq. (3)]. A mass enhancement associated with charged phonons can be expected to be much larger than any mass enhancement in a Fermi liquid.

The system $La_{2-x}Sr_xCuO_4$ allows us to probe to temperatures $T > 300$ K. For $0.12 \leq x \leq 0.21$, the measurements reveal a narrow temperature interval T_l across which the holes gradually change their character; the polarons appear to move independently with a $\Delta H_m = 0$ above T_l, as in the range $0 < x \leq 0.10$. At temperatures $T > T_l$; there appears to be a complete solid solution over the range $0 \leq x \leq 0.30$ with a gradual transition from diffusive to itinerant electron behavior with increasing x. In this model, the $R \sim T$ behavior of the normal state of the superconductor phase does not saturate because the charge carriers are "dressed" and behave as a polaronic gas above T_l, a transition temperature that appears to be controlled by the lattice dynamics rather than by the hole concentration.

We emphasize once more our belief that the normal state of the superconductor compositions in the temperature interval $T_c < T < T_l$ is unusual and, we believe, corresponds to a distinguishable thermodynamic state. We do not offer a theoretical description of this state. However, we reject the marginal Fermi liquid description of Varma[28] and any other description that confines the electron-phonon interactions to the Migdal approximation. We need a theory for a polaron (or Luttinger) liquid in which itinerant electrons are strongly coupled to optical phonons.

Charge carriers cannot remain dressed at high concentrations. The transition from a superconductor to a conventional metal, appears to be characterized at low temperatures by a sharp decrease in T_c with increasing x within the superconductive phase; the system remains an unusual metal to $x = 0.30$ with a metal-metal transition occurring at the step in R vs T near 37 K. Conventional metallic behavior can only occur for $x > 0.30$.

3. Crossover with increasing p from more ionic to covalent Cu-O bonding

At this point, it is instructive to turn to the constructions of Figs. 8 and 9 for the electronic states of the $(CuO_2)^{2-}$ sheets in a parent compound from an "ionic" model. The energy E_I to transfer an electron from a Cu^+ ion to an O^- ion at infinite distance is compensated by the lattice electrostatic Madelung energy E_M associated with formation of the crystal. An $E_M > E_I$ is indicated by the antiferromagnetic, semiconductor character of the parent compounds. The local symmetry of the anion coordination about the Cu atoms of a CuO_2 sheet is in all cases such that the electron removed from the Cu-3d shell is from the x^2-y^2 orbitals that overlap the O-2p_σ orbitals within a CuO_2 plane; these are the most strongly antibonding. So long as $E_M - E_I > 0$ is large enough for the Cu-3d, O-2p_σ covalent bonding to be treated in second-order perturbation theory, the Cu-O covalence can be built into the crystal-field wave function operative for the empty Cu-O antibonding x^2-y^2 orbital of Cu^{2+}-Cu^+ redox couple:

$$\psi_{x^2-y^2} = N_\sigma(f_{x^2-y^2} - \lambda_s\phi_s - \lambda_\sigma\phi_\sigma) , \tag{6}$$

where $f_{x^2-y^2}$ is the Cu:3$d_{x^2-y^2}$ atomic wave function, ϕ_s and ϕ_σ are appropriately symmetrized nearest-neighbor O-2s and O-2p_σ orbitals, and the $\lambda_s, \lambda_\sigma$ are the corresponding covalent mixing parameters

$$\lambda \equiv b^{ca}/\Delta E . \tag{7}$$

The cation-anion electron-energy transfer (resonance) integral b^{ca} is proportional to the overlap integral for the mixing wave functions and ΔE is the energy required to transfer the anion electron back onto the cation. For λ_σ, we have

$$\Delta E_\sigma = (E_M - E_I) \tag{8}$$

and in tight-binding theory; the Cu-O-Cu interactions give a bandwidth for the $\sigma^*_{x^2-y^2}$ band of

$$W \approx 8\varepsilon_\sigma\lambda_\sigma 2 < U , \tag{9}$$

where ε_σ is a one-electron energy. Since the parent compounds are antiferromagnetic insulators, the Cu-O-Cu in-

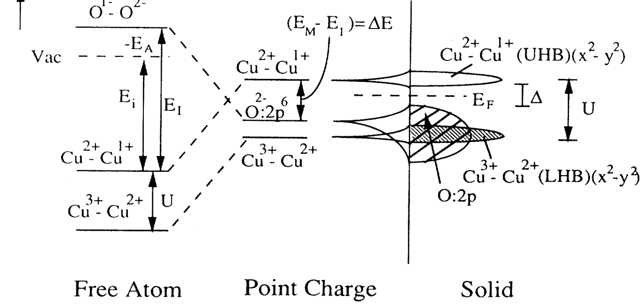
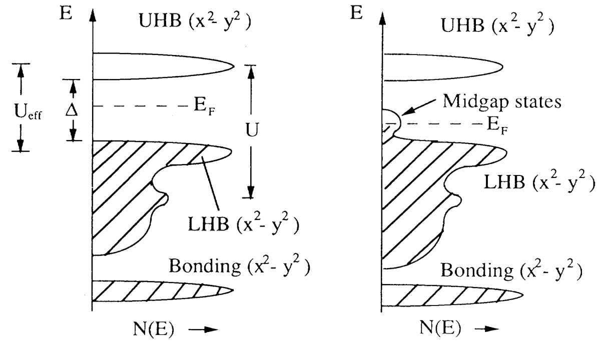


FIG. 8. Construction of the electron energies of the CuO_2 sheets with an ionic model.



(a) (b)

FIG. 9. Schematic density of one-electron states for (a) La_2CuO_4 and (b) $La_{2-x}Sr_xCuO_4$. Note: Spectral weight shifted from upper and lower Hubbard bands (UHB) and (LHB) into midgap states.

teractions are relatively weak, $W < U$, and a $U \approx 5-8$ eV has been estimated.[29] An optical charge-transfer gap $\Delta \approx 2.1$ eV (Ref. 4) therefore places the lower $\sigma^*_{x^2-y^2}$ Hubbard band within the energies of the O-2p bands resulting from O-O interactions as pictured schematically in Fig. 8. However, this picture is misleading. First-order hybridization of the lower $\sigma^*_{x^2-y^2}$ band and the overlapping O-2p states raises to the top of the filled bands strongly hybridized Cu-3$d_{x^2-y^2}$ and O-2p_σ antibonding states of x^2-y^2 symmetry, as illustrated in Fig. 9. These states form an effective lower Hubbard band of antibonding $\sigma^*_{x^2-y^2}$ character and consequently create a $U_{\text{eff}} - W \approx \Delta$; but the much more strongly hybridized character of the states in the lower $\sigma^*_{x^2-y^2}$ band has profound consequences for the physical properties on oxidation of the CuO_2 sheets. With deep oxidation, a bandwidth $W > U$ transforms the ionic model to a covalent model and localized crystal-field orbitals with superexchange Cu-O-Cu interactions to itinerant electron states with conventional metallic behavior. The key to copper oxide superconductors appears to be that they are found at the crossover from ionic bonding in a parent compound to a conventional metal consisting of a partially filled $\sigma^*_{x^2-y^2}$ band with strongly hybridized Cu-3$d_{x^2-y^2}$ and O-2p_σ one-electron states. The transition from ionic to covalent bonding is first order.[30]

Of particular interest to us has been the observation from optical spectroscopy[24] of the appearance of "midgap states" above the top of the lower $\sigma^*_{x^2-y^2}$ band on oxidation of the CuO_2 sheets. Lifting of states out of a narrow band on oxidation is characteristic of small-polaron formation; it signals a "dressing" of the holes with local, cooperative atomic displacements. However, in the copper oxides, the lifting of states from the lower $\sigma^*_{x^2-y^2}$ band into the energy gap is particularly marked (~ 0.5 eV); if it were caused by a local lattice relaxation alone, we should expect to find a $\Delta H_m > 0$ for the hole mobility. We attribute this unusual situation to a change locally from an ionic to a covalent model for the Cu-O bond in the neighborhood of the holes. The discontinuous increase in the Cu-O bond length in the CuO_2 sheets with the first-order loss of interstitial oxygen above 500 K in $La_2CuO_{4.05}$ (Ref. 8) shows the sensitivity of the bond length to the oxidation state in this system. But we need to note that the Hubbard energy U_{eff} also decreases from $U_{\text{eff}} - W \approx 2.1$ eV in the parent compound to a $U_{\text{eff}} < W$ in the conventional metal with $p > 0.30$. Therefore the introduction of midgap states is signaling, in addition to a "dressing" of the holes, a significant change in U_{eff} on passing from a hole-rich to a hole-poor region. This change in U_{eff} follows from the change in O-2p_σ hybridization on going from one domain to the other. These changes are responsible for the metastability of the compositions below T_l in the oxidation-state range $0 < p < 0.12$; what is surprising is that they also appear to stabilize a high-T_c superconductor phase between the parent antiferromagnetic compound, where an ionic model is applicable, and a conventional-metal phase. The existence of unusual electron-phonon interactions in the normal state and a marked change in U_{eff} on going from within to without an atomic displacement "bag" containing Cooper pairs are the essential ingredients of the "correlation-bag" model of high-T_c superconductivity that we have proposed elsewhere.[1]

Another distinctive feature of the compositional ranges $0.05 < x < 0.12$ and $0.15 \le x \le 0.20$ is the magnitude of the isotope effect on replacing O^{16} by O^{18} (Ref. 31). We have already distinguished the superconductive state condensed within charge fluctuations from that condensed from a homogeneous normal state. It has been suggested that there are two distinguishable superconductive mechanisms: a Bose condensation for $0.05 < x < 0.12$ and a BCS pairing for $0.15 < 0.20$ (Ref. 32). We believe that one mechanism is operative and that this one is different from both Bose condensation and pairing by a BCS retarded potential. What is distinguishable is the nature of the normal state from which the Cooper pairs are condensed. Clearly we should anticipate an important isotope effect of the dynamic charge fluctuations that would not be present in a homogeneous normal state.

With such a model, it is imperative to ask whether the transition from ionic to covalent Cu-O bonding can also apply to n-type copper oxide superconductors. To address this question, we refer to the work of Arima *et al.*[4] and Tokura *et al.*[33] These workers have optically measured the charge-transfer gap Δ separating the lower and upper $\sigma^*_{x^2-y^2}$ bands of Fig. 9 for the parent compounds Ln_2CuO_4, Ln=Pr to Gd, of the n-type superconductors having the tetragonal T' structure. In the T' structure, the c axis oxygen of Fig. 1 are displaced to tetrahedral sites between the two Ln planes of the nonsuperconductive layer. This displacement puts the CuO_2 planes under tension, stretching the Cu-O bonds in the planes from their equilibrium value and lowering the oxygen coordination from six to four. The result is a 0.5 eV drop in Δ on going from La_2CuO_4 to Pr_2CuO_4. This drop signals a lowering of the Madelung energy E_M (from Fig. 8):

$$\Delta \approx (E_M - E_I) - W \;, \tag{10}$$

and decreasing the Cu-O bond length would normally be expected to increase W.

As the Cu-O bond length decreases from 1.98 to 1.945 Å on going from Ln=Pr to Gd, Δ increases by over 0.15 eV; the application of hydrostatic pressure on Eu_2CuO_4 also increases Δ linearly with pressure.[33] Expansion of the Cu-O bond length clearly lowers Δ in the T' system, which implies from (10) that the Madelung energy E_M is more sensitive to the Cu-O bond length than to the bandwidth W. Interestingly, pressure decreases Δ in La_2CuO_4, which has an additional apical Cu-O bond. Oxidation of the CuO_2 sheets of La_2CuO_4 shortens the Cu-O bond length and reduces Δ. Reduction of the CuO_2 planes of the Ln_2CnO_4 T' phases increases the Cu-O bond length, which also reduces Δ by reducing E_M. These data indicate that a crossover from an ionic to a covalent model of the Cu-O bond is possible in both the p- and n-type systems, and preliminary measurements indicate that the consequences of such a crossover for electron-lattice interactions and the modulation of ΔU_{eff} is operative in the n-type as well as the p-type copper oxide superconductors.

II. FINAL REMARKS

The theoretical community has addressed the problem of high-T_c superconductivity in the copper oxides from two opposing directions; neither approach has proven totally satisfactory. One approach is to start with an ionic model, which appears to be applicable to the antiferromagnetic parent compounds, and to explore how the system is modified by the introduction of charge carriers under the condition that the Cu^{2+}-Cu^{+} and Cu^{3+}-Cu^{2+} redox couples, which correspond to the upper and lower Hubbard bands in the parent compound (see Figs. 8 and 9), remain split by an on-site electron-electron Coulomb energy U. These studies assume the existence of a continuous solid solution between the parent and superconductor phases; they are made either in the context of strong electron-electron interactions or in that of strong electron-phonon interactions in the mixed-valent states. In the former approach the emphasis is on the interaction of the mobile charge carriers with antiferromagnetic spin fluctuations; in the latter it is on the polaronic character of the charge carriers and their formation of large bipolarons that Bose condense in the superconductive state.

The second approach is to start with a Fermi liquid and Migdal's perturbation approximation for the electron-phonon interactions, which appears to be applicable to the more heavily doped conventional-metal phase, and to explore how the system is modified by the introduction of stronger electron-electron interactions at the superconductor compositions. Low-temperature observations of a complex Fermi surface having a locus in reciprocal space that is in remarkable agreement with band theory predictions[34,35] have been made on a p-type superconductor; this achievement would seem to indicate that Fermi-liquid theory represents a necessary starting point for any low-temperature description of the normal state in the p-type superconductors having the optimum charge-carrier concentration for a maximum value of T_c. On the other hand, the transport properties and the spectroscopically determined densities of states are not predicted by the theory. For example, Fisk and Webb[36] and Gurvitch[37] have argued that at high temperatures, reduction of a narrow-band electron (or hole) mean free path to a lattice-parameter length, causes the curve of resistivity ρ versus temperature T to saturate, and such a saturation is found in the superconductors having the A15 structure; but in the copper oxide superconductors a $\rho \sim T$ is retained to highest temperatures. Varma[28] has developed a "marginal Fermi-liquid" model to account for these properties within the context of strong electron-electron interactions and negligible electron-phonon interactions. However, in this model he is forced to assume a self-energy of unusual form, and it is clear that the applicability of band theory becomes increasingly problematic with decreasing hole concentration. Anderson[38] has marshalled numerous arguments to show that the normal state of the copper oxide superconductors cannot be described by Fermi-liquid theory.

Band theory is not a suitable starting point for the parent compound where the energy gap separating the empty $\sigma^*(x^2-y^2)$ states from the filled $\sigma^*(x^2-y^2)$ states of the $(CuO_2)^{2-}$ sheets has its origins in a Hubbard on-site electron-electron electrostatic energy U that is larger than the width W of the $\sigma^*(x^2-y^2)$ band (see Figs. 8 and 9). Therefore, the p-type character of the superconductive phase is most readily understood as a retention to an important degree of the Hubbard energy U; it is not caused by the opening of a gap at the Fermi surface by a spin-density wave that appears to be the underlying assumption of the "spin-bag" model of Cooper pair formation.[3] However, what is most lacking in the band theory approach to the copper oxide superconductors is an adequate attention to the important role of the electron-phonon interactions; it appears to be necessary to go beyond the perturbation treatment of Migdal's approximation so as to allow the quasiparticles to become "dressed" not only with antiferromagnetic spin fluctuations, but also with cooperative and dynamic local lattice displacements that do not destroy k as a good quantum number. The existence of a measurable Fermi surface in the locus predicted by band theory and the opening of an energy gap at the Fermi energy E_F below T_c clearly argue for the formation of Cooper pairs and against a Bose condensation of bipolarons below T_c.

In this paper, we have presented experimental evidence from two related p-type systems for strong electron-lattice interactions. We have argued that the data indicate the formation of intermediate-size polarons in the compositional range $0<p<0.25$, where p is the concentration of holes per Cu atom in a CuO_2 sheet. At temperatures $T>T_l \approx 300$ K, synthesis of a complete range of solid solutions from an antiferromagnetic parent compound ($p=0$) to a conventional metal ($p>0.30$) may be possible, as in the system $La_{2-x}Sr_xCuO_4$. However, at temperatures $T<T_l$ the system manifests an instability relative to a phase segregation into the parent antiferromagnetic phase and a superconductive phase in the compositional range $0<x<0.12$; in the range $0.12<x\leq 0.20$, the intermediate-size polarons change

from a disordered ensemble moving independently above T_l to an ordered array moving cooperatively below T_l with a meaningful momentum operator k. The intermediate-size polarons have a volume that includes four to five Cu atoms within a CuO_2 sheet and an enthalpy $\Delta H_m = 0$ for motion in the sheet, which gives two-dimensional metallic conduction having a resistance $R \sim T$ in the basal planes. The charge-carrier momentum vector **k** within the superconductive CuO_2 sheets defines a Fermi surface even though the "dressed" holes are not scattered from aperiodicities in the periodic potential like the quasiparticles of a Fermi liquid.[32] The normal state of the superconductive compositions therefore appears to be a distinguishable thermodynamic state intermediate between the antiferromagnetic parent phase and the conventional-metal phase of more heavily doped compositions; its description is not readily accessible from either a purely strong correlation model or a purely weak-correlation model; it embraces a coexistence of the two extremes that requires a distinct theoretical description.

To account for our findings as well as the important optical data of Uchida *et al.*[24] we have pointed out that a crossover from more ionic to covalent Cu-O bonding in the presence of a large on-site electron-electron Coulomb energy U_{eff} creates the conditions for the strong, cooperative electron-lattice interactions needed to obtain intermediate-size polarons. These interactions also transfer spectral weight into the energy gap between the upper and lower Hubbard bands with increasing p, and the unusual mid-IR band appearing at 0.5–0.8 eV is attributed, in our model, to transitions between more ionic and covalent Cu-O bonding. These conditions, which we have argued also apply to the n-type superconductors via a reduced Madelung energy E_M, allow the coexistence of covalent and ionic Cu-O bonding via cooperative, dynamic atomic displacements that modulate the mean Cu-O bond length at the Cu atoms. Moreover, a sharp change (ΔU_{eff}) in the magnitude of the electron-electron repulsive energies on passing from an ionic fluctuation to a covalent domain is able to stabilize the formation of Cooper pairs in the presence of a relatively large average value of U_{eff}.[1]

We have made no attempt to formulate a formal theory for the unusual normal state of the high-T_c superconductors, but we reinforce our position by citing six additional types of experiments that indicate electron-phonon interactions stronger than those of conventional band theory with Migdal's approximation are playing a determining role in both the anomalous normal-state properties and the stabilization of Cooper pairs below T_c.

A. Thermal conductivity

From the temperature dependence of the thermal conductivity below 150 K for different values of x in the systems $La_{2-x}M_xCuO_4$, where $M =$ Sr or Ba, Sera *et al.*[39] have shown that for $x < 0.2$, the thermal current is carried mainly by phonons, but for $x > 0.30$ it is carried mainly by electrons. Cohn *et al.*[40] have measured the anisotropic thermal conductivity in single-crystal $YBa_2Cu_3O_{6.92}$ and concluded that the electron-phonon coupling is larger in $YBa_2Cu_3O_{6.92}$ than in any conventional material.

B. Angle-resolved photoelectron spectroscopy (ARPES)

From the ARPES spectra for the copper oxide superconductors, Sawatzky[41] has estimated that about 90% of the spectral intensity is shifted from the quasiparticle peak to an incoherent continuum, which indicates that the electrons near the Fermi surface are "dressed" with a local distortion caused by the interactions of the individual electrons with their immediate surroundings.

C. Ion channeling

The axial ion channeling mode in Rutherford backscattering (RBS) is highly sensitive to lattice vibrations and small atomic displacements from regular lattice positions. The rms amplitude of the atomic displacements can be derived from the normalized minimum yield $\chi_{\min}$ in the axial channeling. Haga *et al.*[42] have measured the $\chi_{\min}$ of $\langle 011 \rangle$ aligned channeling for each constituent atom of $YBa_2Cu_3O_{7-\delta}$ for temperatures down to 50 K. Enormous changes in the $\chi_{\min}$ values were observed for the Cu and O atoms in a narrow temperature range in the vicinity of T_c; these changes indicate that complicated lattice dynamics of the Cu and O atoms are occurring at and just above T_c.

D. Pair distribution function (PDF)

Atomic PDF's describe the distribution of interatomic distances; a PDF is computed from the Fourier transform of the atom-atom interference function, which incorporates both Bragg and diffuse scattering. Computation of the PDF does not assume either local or translational symmetry. Therefore, in contrast to crystallographic analysis, PDF analysis is able to distinguish between random and correlated atomic displacements that may be dynamic. Toby and Egami[43,44] have performed a PDF analysis of neutron powder-diffraction data obtained from a sample of nominal $Tl_2Ba_2CaCu_2O_8$ having a $T_c = 110$ K; they have demonstrated short-range, correlated atomic displacements in the superconductive CuO_2 planes that are dynamic and change at the onset of superconductivity. The principal oxygen atom displacements were found to occur perpendicular to the CuO_2 sheets. The analysis indicates that atomic-scale, inhomogeneous atomic fluctuations play a critical role in the stabilization of superconductive pairs in the copper oxides.

E. Motional broadening of ^{57}Fe Mössbauer resonance

Wu *et al.*[45] have monitored the temperature dependence of the ^{57}Fe resonance in $YBa_2(Cu_{0.98}Fe_{0.02})_4O_8$ samples and found a discontinuity in the observed linewidth $\Gamma(T)$, isomer shift, and quadrupole splitting at T_c. Below T_c, an excess linewidth $\Delta\Gamma(T)$ increases exponentially with decreasing T with an activation energy $\Delta E_a = 10(1)$ meV in the interval $T_{sc} < T < T_c$ and $\Delta E_a = 1.6(5)$ meV for $T < T_{sc}$. A precipitous drop in the Debye-Waller factor occurs below T_{sc}. In the copper oxide intergrowth structure, an important electric-field gradient is present perpendicular to the CuO_2 sheets that, in the normal state, fluctuates rapidly. In the superconductive state, the correlation time τ_c of the fluctuations apparently increases from a $\tau_c \approx 10^{-12}$ s in the normal state to $\sim 10^{-8}$ s as holes in the planes progressively exhibit Cooper pairing. This behavior indicates the presence of an important coupling between the vibrational and electronic degrees of freedom in the CuO_2 planes.

F. Changes in A_g vibrational modes at and below T_c

Strong electron-phonon interactions are also evident in the abrupt changes in frequency, linewidth, and intensity of all five Raman-active A_g modes at and below T_c.[46,47] In particular, a softening of the B_{1g} mode associated with out-of-phase c-axis displacements of oxygen in the CuO_2 planes has been observed to increase with the number of Cooper pairs formed below T_c; this softening cannot be reconciled with weak-coupling BCS theory.[48] Recent measurements[49] of coherent optical phonons observed in time-domain reflectivity with femtosecond time resolution have allowed observation of the c-axis vibration of Ba (120 cm^{-1}) and Cu(2) (150 cm^{-1}) in $YBa_2Cu_3O_{6+x}$ ($x > 0.9$) films. A nearly constant c-axis motion of the Cu(2) atoms upon cooling down to T_c is followed by a distinct increase at T_c. These observations show that the charge carriers that form Cooper pairs interact strongly not only with the Raman or ir active modes, but also with the high-energy optical modes that modulate the Cu-O bond lengths of the Cu of a CuO_2 plane.

Financial support by the Welch Foundation, the National Science Foundation, and the Texas Advanced Research Program is gratefully acknowledged.

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