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# Vibronic dispersion in the copper oxide superconductors

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Attempts to describe the normal-state electronic behavior of the copper oxide superconductors have been unable to reconcile the following observations: (i) a well-defined Fermi surface with a locus predicted by band theory, but having charge carriers of a sign predicted for a Mott-Hubbard splitting of the band; (ii) a change in sign of the carriers to that predicted by band theory, but without a significant change in the locus of the Fermi surface, on overdoping beyond the narrow superconductive compositional range; (iii) a remarkable stability of the narrow range of superconductive charge-carrier concentrations in the $CuO_2$ sheets even in the presence of charge transfer from nonsuperconductive intergrowth layers; (iv) a dramatic sensitivity of the Néel temperature of the parent compound to oxidation of the $CuO_2$ sheets, but the persistence of antiferromagnetic spin fluctuations into the superconductive compositions; and (v) unusual transport properties that cannot be treated within the Migdal approximation and are insensitive to high magnetic fields. To address this impasse, we propose a phenomenological polaron model based on the observation that the system must accommodate to the coexistence of "ionic" and "covalent" Cu-O bonding having different equilibrium Cu-O bond lengths. We designate this entity a *correlation* polaron. Covalent Cu-O bonding with molecular-orbital formation occurs within the polaron, which moves in a background of ionic Cu-O bonding. Vibronic coupling at the "avoided crossover" from ionic to covalent bonding allows diffusional motion of uncoupled polarons without any motional enthalpy in the mobility. At temperatures $T > T_l \gtrsim 300$ K the polarons are uncoupled and move randomly; in the narrow superconductive compositional range they condense below $T_l$ to form a distinguishable thermodynamic phase consisting of extended vibronic states. In this "polaron liquid," a distinction between bonding and antibonding states within the polarons opens a gap at the half-band position, not the Fermi energy, and some spectral weight associated with the ionic Cu-O bonding still remains at the energies of the upper and lower Hubbard bands of the parent compound.

## I. INTRODUCTION

Description of the conduction electrons in the normal state of the copper oxide superconductors remains a central challenge for any theory of their high-$T_c$ superconductivity. Serious attempts to obtain a quantitative theory have been made from three different starting points; each has had success in describing some features, but none has proven totally satisfactory. We suggest here a fourth alternative that is conceptually a radical departure from conventional solid-state models, and we argue why we believe it may prove a more useful starting point for a quantitative theory. But first we review briefly what we believe to be major successes and shortcomings of theories based on the three more conventional starting points.

### A. Fermi-liquid theory

Although band theorists have used the local-density approximation and Fermi-liquid theory (FLT) to obtain excellent agreement on the location of an experimentally well-defined Fermi surface within momentum space,[1,2] their calculations give a poor fit to the measured electron-energy dispersion near the Fermi energy,[3,4] particularly for the $n$-type superconductors,[5] and the photoelectron peaks obtained by angle-resolved photoelectron spectroscopy (ARPES) are disturbingly broader than predicted by theory.[4] Moreover, band theory predicts that the $p$-type superconductors should be $n$ type and the $n$-type should be $p$ type. The correct sign of the charge carriers is only found in the "overdoped" materials where the high-$T_c$ phenomenon is suppressed.[6] Also, FLT is not able to account for a number of other physical properties.[1,7] For example, antiferromagnetic spin fluctuations persist to the highest temperatures,[8] and the resistivity of the optimum superconductive compositions is anomalous both for its large value and for a linear temperature dependence that fails to saturate at high temperatures.[9] Where electron-phonon interactions can be treated within the Migdal approximation, the resistivity $\rho$ saturates at higher temperatures; in the $A15$ superconductive alloys, for example, the resistivity never exceeds a 120 $\mu\Omega$ cm limit.[10] Lack of any saturation of $\rho$ in the copper oxides implies either extremely weak electron-phonon interactions, which many experiments show to be not the case,[11] or a transport process incompatible with the Boltzmann equation. Moreover, in conventional superconductors where the BCS superconductive condensation requires Cooper pairing of the quasiparticles of FLT, the resistivity obeys a $\rho \sim T^2$ law in the temperature range $T_c < T < T_H$; $T_H$ is the characteristic temperature below which FLT applies. In the high-$T_c$ superconductors, the critical temperature $T_c$ occurs as high as 125 K in a temperature range where $\rho \sim T$. We are forced to ask

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what distinguishes the electron-phonon interactions in the copper oxides from those in the metallic alloys.

### B. Hubbard models

An alternative approach is to start with the observation that the parent compounds are antiferromagnetic insulators, which signals that the electrons of the half-filled antibonding (with respect to the Cu-O interactions) $\sigma^*$ bands of $x^2-y^2$ parentage on the $CuO_2$ sheets are strongly correlated by an on-site electron-electron Coulomb energy $U$ that splits the half-filled band into an upper and a lower Hubbard band, the UHB and LHB, respectively. This splitting of the half-filled band provides a natural explanation for $p$-type conduction where the antiferromagnetic $CuO_2$ sheets are oxidized, $n$-type conduction where they are reduced.

Starting from this strong-correlation limit in which the $x^2-y^2$ bandwidth is $W < U$, theorists have adopted two different limiting assumptions for the discussion of mobile charge carriers introduced by oxidation or reduction of the antiferromagnetic $CuO_2$ sheets. One school assumes that the electron-phonon interactions are extremely weak and concentrates on the electron-electron interactions, incorporating the role of the electron spin and the interatomic spin-spin exchange interaction; the other assumes that strong electron-phonon interactions dominate through the postulate of large polaron charge carriers.

#### *1. Weak electron-phonon interactions*

Restriction of the problem to electron-electron interactions allows retention of itinerant-electron (though perhaps only as a Luttinger liquid) behavior as long as the charge carriers move within a coherent antiferromagnetic state,[12] a resonating-valence-bond (RVB) state,[13] or a spin-density-wave (SDW) state.[14] This approach is consistent with the observation of spin fluctuations persisting into the superconductive compositions,[8] and some models, (e.g., Ref. 14) predict the observed[15] $d$-wave symmetry for the superconductive Cooper pairs. Moreover, the breadths of the photoelectron peaks near $E_F$ in ARPES appear to be more compatible with a Luttinger liquid than with a Fermi liquid. On the other hand, there are considerable data indicating the presence of strong electron-phonon interactions[11] that this approach ignores. Moreover, a failure to observe any deviation of the Seebeck coefficient under magnetic fields to 30 T (Ref. 16) is troublesome, as indeed is the character of the Seebeck coefficient itself.

#### *2. Conventional polarons*

We distinguish a *conventional* polaron from a *spin* polaron and from a to-be-defined *correlation polaron.* A conventional polaron is defined as a charge carrier in a mixed-valence system that is self-trapped in a local region of space by inducing a local lattice deformation. A spin polaron is such a charge carrier in a paramagnetic system that is self-trapped by inducing a short-range ferromagnetic ordering. A correlation polaron is here defined as such a charge carrier in a strongly correlated system (large effective Hubbard U for the parent single-valence compound) that is self-trapped by inducing, in addition to a local lattice deformation, a sharp reduction of the correlation energy $U$ within a short-range region of real space.

The local lattice deformation induced by a conventional polaron raises a single hole state per $p$-type charge carrier above the top of the highest occupied band; it lowers a single occupied state per $n$-type charge carrier below the bottom of the lowest unoccupied band. The conventional-polaron model cannot account for the transfer of excess spectral weight per charge carrier into the charge-transfer gap that is observed[17] in the copper oxide superconductors.

Where the conventional polaron is trapped at a single site of a like-atom array, including the unlike near neighbors, it is classified as a small polaron. Small polarons move diffusively through the lattice; therefore, they generally have an activated mobility, which gives a semiconductive temperature dependence of the resistivity. Such a model cannot apply to the copper oxide superconductors.

Where the conventional polaron is weakly self-trapped in a domain consisting of several like atoms, it is classified as a large polaron. Under a number of assumptions, a large polaron can be treated as an itinerant species having a well-defined momentum vector **k**. In the calculation of Schüttler and Holstein,[18] for example, the assumptions used include elastic electron-lattice interactions, a lattice deformation treatable within a continuum-medium model, adiabatic conditions, and a scattering process described by the Boltzmann equation. A condition that must be fulfilled for large-polaron formation is a static dielectric constant $\epsilon_0 > 2\epsilon_\infty$, where $\epsilon_\infty$ is the optical dielectric constant. Emin[19] has tested this condition and several others to show that the copper oxide superconductors should contain large polarons rather than small polarons. Moreover, he has pointed out that suppression of the superconductivity in the "overdoped" region finds a natural explanation with a model of superconductivity that is based on the formation of bipolarons in the normal state. However, the Seebeck data for the underdoped $La_{2-x}Sr_xCuO_4$ system is temperature independent above 240 K and decreases in magnitude with increased doping typical of a diffusive character for the charge carriers.[20–22] The large magnitude of the Seebeck coefficient ($\alpha > 40$ $\mu$V/k) is also typical of a thermoelectric power that is dominated by a statistical contribution; such a large value of $\alpha$ has not yet been found associated with itinerant charge carriers. On the other hand, the temperature variation of the Seebeck coefficient for the optimally doped and overdoped samples changes below room temperature to a behavior characteristic of a strongly mass-enhanced, itinerant charge carrier. Yet in this regime the conventional-polaron model does not address the change in sign of the charge carriers on passing from the superconductive to the overdoped phase.[6] A change in the sign of the Seebeck coefficient near room temperature in an optimally doped superconductor has been predicted[19] with a conventional large-(bi)polaron model, but such a change in sign is only observed experimentally in systems where there is a contribution from a charge-reservoir layer. Use of the adiabatic condition eliminates any possibility in this model of collapsing the large splitting $U$ between the lower and upper Hubbard bands, and so the charge carriers are confined to a small region near the Brillouin-zone boundary; photoemission studies[3,4] place the Fermi surface (or the cutoff energy for bipolarons) near the middle of the Brillouin zone as predicted by band theory. Even an analysis, based on Boltzmann transport, of single-crystal resistivity data would indicate a large Fermi surface.[9]

Finally, advocates of a conventional-polaron model have felt obliged to treat the superconconductivity as a Bose condensation of large bipolarons, and so they have postulated the existence of large bipolarons in the normal state. However, there is little evidence for the existence of bipolarons above the critical temperature $T_c$, and there is convincing evidence for the removal of states from the Fermi energy $E_F$ below $T_c$ as predicted for Copper-pair formation.[4] Failure to open up completely an energy gap, some states remaining near $E_F$, need not require a gapless superconductivity mechanism.

### C. Summary

A satisfactory description of the electrons in the normal state of the copper oxide superconductors is seen to require the meeting of several apparently contradictory constraints on the electrons of the superconductive $CuO_2$ sheets. These constraints include (i) a well-defined Fermi surface with a locus predicted by band theory, but with an electron-energy dispersion that is too narrow and photoelectrons peaks near $E_F$ in ARPES that are too broad for FLT, (ii) parent compounds with antiferromagnetic, insulating $CuO_2$ sheets that become $p$-type conductors on oxidation and $n$-type conductors on reduction and yet exhibit a Fermi surface locus that remains little changed on passing from $p$ to $n$ or $n$ to $p$ conductors with suppression of the superconductive phase by overdoping, (iii) a dramatic sensitivity of the Néel temperature of the parent compound to oxidation of the $CuO_2$ sheets, but the persistence of antiferromagnetic spin fluctuations into the superconductive compositions, and (iv) transport properties that are insensitive to high magnetic fields (contrary to expectations for spin-spin scattering where electron-phonon interactions are weak), which cannot be treated within the Migdal approximation for electron-phonon interactions and which cannot be reconciled with a well-defined Fermi surface located near the center of the Brillouin zone if the charge carriers are conventional polarons or bipolarons.

This impasse indicates the need for a conceptually new starting point. For this purpose, we introduce the concept of a correlation polaron of intermediate size applicable to charge carriers introduced by oxidation of a spin-$\frac{1}{2}$ parent compound described by a Hubbard model with a charge-transfer energy gap. Furthermore, we point out that condensation from a polaron gas to a polaron liquid below a transition temperature $T_l \gtrsim 300$ K can introduce the dispersion necessary to account for a large Fermi surface with a midband gap. In addition, a polaron liquid would make the normal state of the superconductive phase thermodynamically distinguishable from the antiferromagnetic parent phase and the overdoped metallic phase at temperatures $T < T_l$. Application of the model to the $n$-type superconductors requires a reduction of the Madelung energy.[23] We confine ourselves here to the $p$-type superconductors.

## II. POLARON-LIQUID MODEL

### A. Motivation

Examination of several families of copper oxide superconductors led one of us[24] to the conclusion that the superconductive compositions with optimum critical temperatures for a particular system all have mixed-valence $CuO_2$ sheets with charge-carrier concentrations in the range $0.10 \leq p \leq 0.22$, and an independent assessment[25] has recently presented in a more dramatic manner this same conclusion. For us, the significance of this finding is its suggestion that at lower temperatures the superconductive phase is thermodynamically distinguishable from the parent antiferromagnetic-insulator phase on the one side and the overdoped metallic phase on the other.[20] The idea of a thermodynamically distinguishable stable phase was germinated by the observation that the optimum charge-carrier concentration in the $CuO_2$ sheets tends to be stabilized even in the presence of charge transfer between the $CuO_2$ sheets and any charge reservoir in the nonsuperconductive intergrowth layers. In order to demonstrate this idea, we undertook a careful study of the $La_{2-x}Sr_xCuO_4$ phase diagram of Fig. 1,[20,21,26] which we developed in concert with a phase diagram for $La_2CuO_{4+\delta}$.[27,28]

The $La_2CuO_{4+\delta}$ system exhibits a classic spinodal decomposition into an antiferromagnetic and a superconductive phase in the interval $0 < \delta < 0.05$ below 320 K; this phase segregation is made possible by an extraordinary mobility of the interstitial oxygen atoms that allows oxygen diffusion down to 200–220 K.[29,30] This phase segregation reinforces our suggestion that, below 320 K, the antiferromagnetic parent phase and the superconductive phase are thermodynamically distinguishable. Although an ordering of the interstitial oxygen atoms in the superconductive phase found for $\delta \geq 0.05$ makes difficult an unambiguous assessment of the origin of the driving force for the phase segregation, recent experiments[28] show that the phase segregation is electronically driven. Moreover, a characteristic thermal evolution of the resistance and Seebeck coefficient through the temperature range of spinodal segregation allows interpretation of the resistance and thermopower data for compositions $0 < x < 0.10$ in the system $La_{2-x}Sr_xCuO_4$ as indicative of a dynamic phase segregation of the antiferromagnetic and superconductive phases below 150 K.[20,21]

The system $La_{2-x}Sr_xCuO_4$ provides the best opportunity to test any theory because it exhibits a complete evolution from the underdoped to the overdoped regime and contains a single superconductive $CuO_2$ sheet without the complication of a charge-reservoir intergrowth. As shown in Fig. 1, a complete solid solution of $La_{2-x}Sr_xCuO_4$ stoichiometic in oxygen content can be prepared over the range $0 \leq x \leq 0.35$. However, at temperatures $T \leq 300$ K, the temperature dependences of the resistance and thermoelectric power found in the range $0 < x \leq 0.10$ are quite different from those found for $x > 0.10$.

In the range $0 < x \leq 0.10$, the Seebeck coefficient $\alpha$ is nearly temperature independent from highest temperatures down to a $T_F \approx 240$ K. A temperature-independent $\alpha$ having a large magnitude indicates that the statistical term dominates the transport term as occurs with diffusive small-polaron motion. However, interpretation of the magnitude of $\alpha$ is not consistent with a small polaron; it requires a polaron consisting of about five copper atoms and their nearest-neighbor oxygen atoms, which implies a large (or intermediate-size) polaron. Moreover, a $\rho \sim T$ means there is no activation energy in the mobility. Nevertheless, the temperature independence of $\alpha$ as well as an analysis of the single-crystal conductivity data in this compositional range[9] cannot be reconciled with Boltzmann transport. Therefore we are forced to consider the possibility of an unconventional polaron having a size comparable to that of a conventional large polaron, but one that moves diffusively with a motional enthalpy $\Delta H_m = 0$ for which the assumptions (viz., elastic electron-lattice interactions, adiabatic conditions, a scattering process described by the Boltzmann equation, and a lattice treatable as a continuous medium) used to describe a conventional large polaron are not applicable. For reasons discussed below, we designate this unconventional polaron to be a *correlation polaron.*

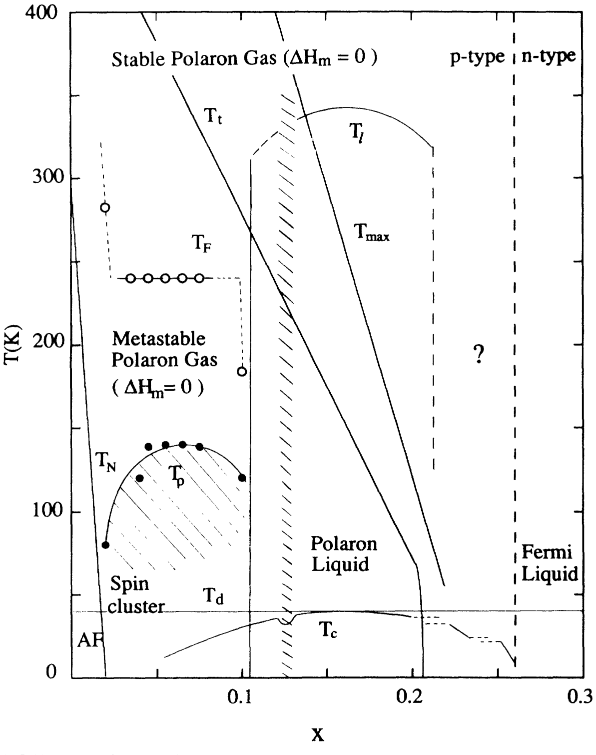

FIG. 1. Phase diagram for the system $La_{2-x}Sr_xCuO_4$, after Refs. 21 and 40. $T_N$=Néel temperature, $T_{\max}$=temperature of maximum susceptibility, $T_t$=orthorhombic-tetragonal transition temperature, $T_c$=superconductive critical temperature, $T_l$=temperature of transition from a polaron liquid (or metastable polaron gas) to a stable polaron gas, $T_\rho$=onset temperature for charge fluctuations that segregate nearly polaron-free from polaron-liquid domains, and $T_F$=crossover temperature below which the spin-fluctuation time is longer than the hole-transfer time ($\tau_F > \tau_h$).

Below $T_F \approx 240$ K in the range $0 < x < 0.10$, $\alpha$ decreases with decreasing temperature, but the change in $d\alpha/dT$ is not reflected in a change in $d\rho/dT$, which remains constant through $T_F$. We have interpreted this change in $\alpha$ within the framework of the statistical contribution to $\alpha$ being dominant; it can arise in a two-dimensional paramagnetic system where short-range antiferromagnetic spin fluctuations become slower than the time for a diffusively moving polaron to hop from one position to a neighboring position. Below $T_\rho < T_F$, the resistivity increases with decreasing $T$, whereas an $\alpha \sim T^{1/2}$ continues to decrease. The changes found below $T_\rho$ are similar to those occurring in $\rho$ and $\alpha$ through the range of spinodal decomposition in $La_2CuO_{4+\delta}$. Since no ions are mobile at temperatures $T < 300$ K in the oxygen-stoichiometric system $La_{2-x}Sr_xCuO_4$, any intrinsic instability of compositions in the range $0 < x < 0.10$ at temperatures $T < 300$ K can only manifest itself through cooperative atomic displacements. Consequently, we have interpreted the changes in $\rho$ and $\alpha$ below $T_\rho$ in the range $0 < x < 0.10$ to signal the stabilization of cooperative atomic displacements that segregate the system into hole-rich superconductive domains and hole-poor antiferromagnetic domains within a $CuO_2$ plane. The fact that $T_c$ increases with $x$ in the compositional range where these charge fluctuations occur, in apparent contradiction of the Gibbs phase rule, is assumed to reflect the dependence of $T_c$ on the mean volume of a hole-rich superconductive domain.[21] Moreover, failure to observe these displacements with neutron diffraction suggests a dynamic phase segregation by short-range charge fluctuations in a $CuO_2$ plane.

A static phase segregation in $La_2CuO_{4+\delta}$ and a dynamic phase segregation in $La_{2-x}Sr_xCuO_4$ between the antiferromagnetic parent phase and the superconductive phase would indicate that the polarons change their character below 300 K in the normal state of the superconductive phase. We are thus led to postulate that in the superconductive compositional range the correlation polarons interact strongly enough to condense, below a $T_l$, into a polaron liquid, but not strongly enough to annihilate polaron formation as occurs in the metallic phase of the overdoped region. The dynamic phase segregation to a superconductive rather than a metallic phase in the underdoped region would appear to signal a relative stability of the polaron-liquid phase, which can only exist in a narrow range of polaron concentrations at temperatures $T < T_l$. According to this model, the character of the polaron liquid would be made manifest at temperatures $T_c < T < T_l$ in a narrow compositional range where only the superconductive phase is present. From the Meissner effect, the range of single-phase bulk superconductivity is confined to $0.10 < x \leq 0.22$ in the $La_{2-x}Sr_xCuO_4$ system and to $\delta > 0.05$ in the $La_2CuO_{4+\delta}$ system. Also, the resistance and thermopower measurements show no evidence of a $T_\rho$ below which a dynamic phase segregation is occurring in this compositional range.

In the ranges $0.10 < x \leq 0.22$ and $\delta > 0.05$ of the $La_{2-x}Sr_xCuO_4$ and $La_2CuO_{4+\delta}$ systems, the temperature dependence of $\alpha$ changes shape from a nearly temperature-independent behavior at $T > T_l$ to a remarkable and characteristic increase with decreasing $T$ through a maximum value near 150 K. The shape of the $\alpha$ versus $T$ curve below 300 K resembles that of the universal function used by Kaiser[31] to describe a mass enhancement of the transport contribution to the Seebeck coefficient. The universal function can only apply where there is a dispersion curve that is strongly modified near $E_F$ by becoming more flat. In conventional alloys, the mass enhancement gives a relatively shallow maximum in the term added to the Mott transport term in $\alpha$ compared to the temperature dependence of $\alpha$ observed in the high-$T_c$ materials. We conclude that the $\alpha$ versus $T$ curve signals a $T_l \approx 300$ K and that the temperature dependence of $\alpha$ below $T_l$ indicates the introduction into $\alpha$ of a large mass enhancement of the relatively small transport term already present above $T_l$ without loss of the identity of the polarons, which continue to give an important statistical contribution. What appears to be a large mass enhancement of the transport term indicates a dispersion curve below $T_l$ that remains nearly flat at $E_F$.

In the range $0.22 < x < 0.28$, the transition to the overdoped phase appears to progress via a series of discrete superconductive phases suggestive of a discrete series of polaron liquids for different hole concentrations with dynamic charge fluctuations separating superconductive domains from more hole-rich metallic domains.[32]

A $\rho \sim T$ is consistent with such a model. However, if the high-$T_c$ superconductive state is condensed from the normal state of a polaron liquid, then $T_l$ must be an upper bound for the formation below $T_f$ of superconductive pair fluctuations. The critical temperature $T_c$ for zero resistance, on the other hand, appears to occur at a $T_c \leq T_d$, where lattice adjustments at $T_d$ allow a change from two-dimensional to three-dimensional (or at least coupling between pairs of $CuO_2$ planes) electronic conduction for $T < T_d$. What structural factors determine $T_l$, $T_d$, and the onset temperature $T_f$ for pair fluctuations remains an open question.

The phase diagram of Fig. 1 is further complicated near $x = \frac{1}{8}$ by a competitive phase; this competitive phase appears to be a commensurate charge-density-wave (CDW) state also stabilized by cooperative atomic displacements. Cooperative atomic displacements associated with a static CDW or a molecular-cluster configuration are known to trap out charge carriers by opening a gap in the density of one-electron states at the Fermi energy $E_F$. Such atomic displacements compete with a superconductive state in which superconductive pairs are stabilized by the removal of states from the neighborhood of $E_F$. This situation is illustrated in the perovskite systems $BaBi_{1-x}Pb_xO_3$ (Ref. 33) and $Ba_{1-x}K_xBiO_3$ (Ref. 34); it is probably responsible for the suppression of superconductivity at $x = \frac{1}{8}$ in the $La_{2-x}Ba_xCuO_4$ system.[35] Any cooperative atomic displacements occurring within the normal state of the superconductive phase that are associated with the proposed correlation polarons, whether as a gas or a liquid, are clearly distinguishable from those that suppress superconductivity. This deduction is reinforced by the observation that a superconductive composition $x = 0.16$ in the system $La_{2-x}Ba_xCuO_4$ segregates below 950 °C via cation diffusion into two nonsuperconductive phases, an $x = \frac{1}{8}$ phase and an overdoped metallic phase.[36] Clearly, the cooperative atomic displacements occurring at $x = \frac{1}{8}$ must be distinguishable from those we postulate to be present in the superconductive phase.

It is significant that above $T_l$ a segregation of the superconductive phase occurs, whereas below $T_l$ the observed phase segregations are to the superconductive phase. Apparently condensation of the polarons into a polaron liquid below $T_l$ stabilizes the superconductive phase.

These data thus provide evidence not only for a thermodynamically distinguishable superconductive phase stabilized at temperatures $T < T_l$, but also for strong electron-lattice interactions that are unusual because they stabilize a dynamic rather than a static coupling. A strong, but dynamic electron-lattice coupling is associated with "vibronic" stabilizations. Vibronic stabilizations in the solid state are encountered in the orbitally degenerate, localized electronic configurations associated with a dynamic Jahn-Teller distortion;[37] in the copper oxide superconductors, we must identify an alternate mechanism for the stabilization of vibronic states.

### B. Ionic versus covalent Cu-O bonding

As discussed elsewhere,[21,23,26] we treat the antiferromagnetic-insulator parent compound within an ionic model in which the antibonding (with respect to Cu-O interactions) state for the $3d$ hole at a formally $Cu^{2+}$ ion has the O-$2p$ and O-$2s$ covalent admixture treated in second-order perturbation theory:

$$\psi_{x^2-y^2} = N_\sigma(f_{x^2-y^2} - \lambda_\sigma\phi_\sigma - \lambda_s\phi_s) , \quad (1)$$

where $f_{x^2-y^2}$ is the atomic $x^2-y^2$ $3d$ orbital with $x$ and $y$ axes directed toward nearest-neighbor copper atoms of a $CuO_2$ sheet. The $\phi_\sigma$ and $\phi_s$ orbitals are appropriately symmetrized O-$2p_x$,$2p_y$ and O-$2s$ orbitals that $\sigma$ bond with $f_{x^2-y^2}$, and

$$\lambda_\sigma \equiv b_p^{ca}/\Delta E_p, \quad \lambda_s \equiv b_s^{ca}/\Delta E_s \quad (2)$$

are the conventional covalent-mixing parameters in which the $b^{ca}$ are the electron-energy-transfer matrix elements to take an electron from an $O^{2-}$ ion to a neighboring $x^2-y^2$ $3d$ orbital on copper and the $\Delta E$ are the energy gaps between the overlapping copper and oxygen states.

In this model, an energy dispersion is introduced via the ca. 180° Cu-O-Cu interactions in the $CuO_2$ sheets; the tight-binding bandwidth is

$$W \approx b^{cac} \sim \epsilon_\sigma(\lambda_\sigma^2 + \lambda_s^2) , \quad (3)$$

where $b^{cac}$ is the electron-energy-transfer matrix element for transfer of an $x^2-y^2$ electron from one copper atom to an $x^2-y^2$ orbital on a neighboring copper atom. In the parent copper oxides containing only $Cu^{2+}$ ions in $(CuO_2)^{2-}$ sheets, the bandwidth $W$ is small compared to the on-site Coulomb repulsive energy $U \approx 5-8$ eV between electrons of the half-filled $x^2-y^2$ band, and $U$ splits the band into upper and lower Hubbard bands (UHB and LHB) as illustrated schematically in Fig. 2(a). In $La_2CuO_4$, a charge-transfer gap $\Delta < U$ places the LHB below the top of the O-2$p$ bands of the ionic model. However, hybridization between the LHB and the O-2$p$ states lifts the antibonding $x^2-y^2$ LHB to the top of the occupied bands to make $\Delta \approx U_{\text{eff}}$ as shown in Fig. 2(b). From optical spectra[38] we obtain a $U_{\text{eff}} \approx 2.0$ eV separating the maximum densities of states in the LHB and UHB. We represent in Fig. 3(a) the dispersion curves for the upper and lower Hubbard bands.

A $\Delta < U$ means that holes introduced into the LHB by oxidation of the $CuO_2$ sheets cannot be treated within the ionic model as the $\Delta E_p$ of Eq. (2) for the equilibrium reaction

$$Cu^{3+}\text{-}O^{2-} = Cu^{2+}\text{-}O^{-} \tag{4}$$

has become negative so as to bias the reaction to the right. As Berry[39] has pointed out, shifting of reaction (4) from a left-hand to a right-hand bias shortens the equilibrium Cu-O bond length; the left-hand "ionic" configuration has a longer equilibrium Cu-O bond length than the right-hand "covalent" configuration. Burdett[40] has recently argued that at crossover the double-well potential may be stabilized by vibronic coupling into a single well. However, in a mixed-valence situation, we should expect rather a segregation into hole-rich domains with covalent bonding and hole-poor domains with ionic bonding, but with a vibronic coupling that allows the polaron to move diffusively without a motional enthalpy one polaron diameter in the period of a lattice vibration. Such a motion gives our estimate of the size of the polaron from the magnitude of the statistical contribution to $\alpha$. The vibronic coupling represents a resonance between the covalent and ionic Cu-O bonding that occurs for $\Delta E_H = \frac{1}{2}U + \Delta E_{\text{el}}$, where $\Delta E_H$ is the gain in hybridization energy, $\Delta E_{\text{el}}$ is the loss of elastic energy, and $\frac{1}{2}U$ enters because of the collapse of the on-site energy $U$ in the molecular orbitals of $x^2-y^2$ symmetry. For a double-well potential, $\Delta E_{\text{el}}$ may be quite small. Thus we postulate that the initial holes introduced are trapped within a mobile volume of covalent Cu-O bonds embedded in a background of ionic Cu-O bonds; the mobile volume of covalent Cu-O bonds constitutes an intermediate-size polaron within which the correlation splitting $U$ is sharply reduced relative to that of the more ionic matrix in which it is embedded. Therefore we refer to it as a *correlation* polaron. No spontaneous magnetism is associated with the electrons in molecular orbitals (MO's) within the polaron volume, and the size of the mobile polarons suppresses the long-range antiferromagnetic ordering temperature $T_N$ much more rapidly than occurs with a dilution by a nonmagnetic species. Cho *et al.*[41] have deduced from nuclear quadrupole resonance

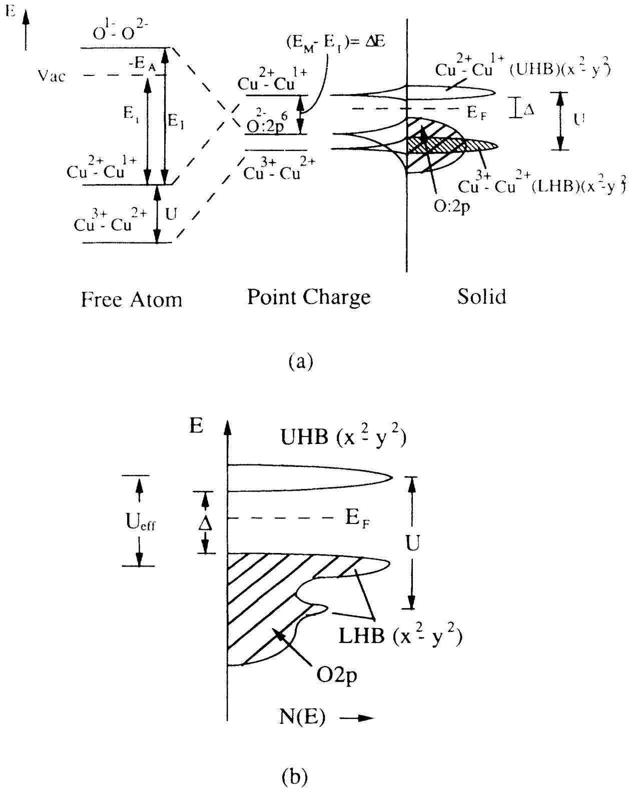

FIG. 2. Ionic model for $CuO_2$ plane of $La_2CuO_4$ (a) before and (b) after hybridization of lower $x^2-y^2$ orbitals with the O-2$p$ bands. $E_M$=Madelung energy, and $E_I = E_i - E_A$ =energy to shift electrons from $Cu^+$ to $O^-$ at infinite separation.

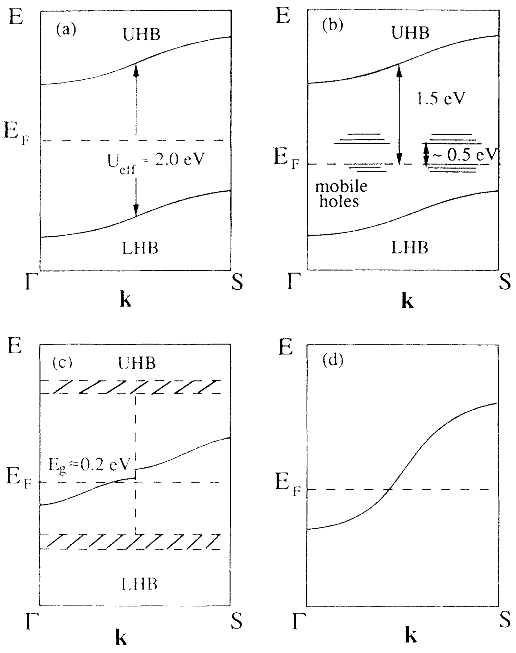

FIG. 3. Schematic dispersion curves for $La_{2-x}Sr_xCuO_4$: (a) $x=0$, (b) $0<x<0.10$, (c) $0.10 \leq x \leq 0.22$, and (d) $x>0.28$.

that the destruction of long-range magnetic order leads to a quasistatic antiferromagnetic background within which nonmagnetic polarons of intermediate size are mobile.

We emphasize here that the transition from "ionic" to "covalent" bonding is not merely a failure of the second-order perturbation theory defined in Eqs. (1)–(3); it represents a first-order transition from one equilibrium Cu-O bond length to another. Moreover, the on-site correlation energy $U$ associated with the longer "ionic" Cu-O bonds collapses in the MO domains of the "covalent" Cu-O bonds because of the much stronger O-$2p_\sigma$ character in the MO wave functions. Whereas this first-order change may be observed directly in a single-valence system such as $NdNiO_3$,[42] it gives rise to a phase segregation in a mixed-valence system. In the copper oxides, this phase segregation manifests itself in the stabilization of the correlation polaron, and a calculation of Yonemitsu, Bishop, and Lorenzana[43] describes a crossover from a Zhang-Rice ionic regime to a covalent MO regime having no correlation splitting of the states within the polaron. However, there is a splitting between the Cu-O-Cu bonding and antibonding MO states. We emphasize further that the first-order character of the phase change between covalent Cu-O bonding within and ionic Cu-O bonding without a correlation polaron means that the assumptions used to describe a conventional large polaron are not applicable to the correlation polaron. Clearly, the electron-lattice interactions are not elastic, the medium is no longer a continuum, Boltzmann scattering cannot be used to describe polaron transport, and the system is not adiabatic.

At temperatures $T > T_l$, the Seebeck and resistivity data also support such a model for a correlation polaron of intermediate size with no motional enthalpy in the mobility. However, the model rests on the contention that the Cu-O bond length places the equilibrium reaction (4) near to the crossover condition. Near crossover, we must anticipate an exceptionally large compressibility of the Cu-O bond where there is a large concentration of ionic Cu-O bonds. Available direct data on the Cu-O bond length versus pressure indicates that the bond is indeed highly compressible;[44,45] indirect evidence comes from the pressure dependence of the orthorhombic-tetragonal transition temperature $T_t$ in this system.[32] As one of us has argued elsewhere,[46] the orthorhombic distortion occurs to relieve the compressive stress on the $CuO_2$ sheets created by a bond-length mismatch between the LaO-LaO rocksalt bilayers and the $CuO_2$ sheets. The mismatch is represented by the tolerance factor

$$t = \text{La-O}/\sqrt{2}(\text{Cu-O}) \qquad (5)$$

for the tetragonal structure, where La-O and Cu-O represent equilibrium bond lengths that vary with temperature and pressure. The orthorhombic distortion relieves the mismatch associated with a $t < 1$, which decreases with decreasing temperature because of the larger thermal expansion of the La-O bond. In many $ABO_3$ perovskites, pressure has been used to control which hexagonal polytype is stabilized for a $t > 1$; advantage is taken of the larger compressibility of the $A$-O bond to stabilize under pressure more cubic stacking.[47] Applying the same reasoning, pressure should stabilize the orthorhombic phase relative to the tetragonal phase in the $La_{2-x}Sr_xCuO_4$ system if the La-O bond is the more compressible. The fact that the tetragonal phase is stabilized signals that in this system the Cu-O bond is the more compressible, which can only occur if the Cu-O bond has unusually high compressibility.

### C. Polaron coupling

At temperatures $T > T_l$, the correlation polarons move randomly for all $x < 0.35$. For random, diffusive motion, the holes do not see the translational symmetry of the lattice, and so they have no **k** quantum number and no energy dispersion. The holes states are lifted out of the LHB as for a conventional small polaron, but occupied MO states within the volume of the intermediate-size polaron are also formed from the UHB and LHB, which transfers excess spectral weight into the correlation gap because of the collapse of $U$ associated with the MO's of the polaron (of course, there is also the excess transfer of spectral weight associated with a strongly correlated system). In support of this latter formation of MO states is the observation from photoelectron spectroscopy of the transfer of excess spectral weight from the Hubbard bands to the Hubbard gap.[17] The appearance upon doping of an optical absorption centered at about 0.5 eV places the polaron hole at an energy 0.5 eV above the maximum density of states of the LHB as indicated schematically in Fig. 3(b). Placement of the polaron energy above the top of the LHB restricts the width of the LHB to $W < 1.0$ eV, which is consistent with a $W < U_{\text{eff}} \approx 2.0$ eV.[38]

At temperatures $T < T_l$, we must distinguish between the compositional ranges $0 < x < 0.10$, $0.10 \leq x \leq 0.22$, and $0.22 < x < 0.30$. In the range $0 < x < 0.10$, the polaron-polaron interactions are weak and the polaron motions move randomly and independently down to $T_\rho$, the temperature below which charge fluctuations stabilize a dynamic segregation into antiferromagnetic domains and superconductive domains; within the superconductive domains, the polaron concentration is large enough for strong polaron-polaron interactions to stabilize a new type of electronic state. Lorenza and Yu[48] have recently argued from a $p$-$d$ model for an evolution with $x$ from a polaron to an itinerant-electron regime and have estimated that the coupling between polarons begins to become important at $x \approx 0.10$ in $La_{2-x}Sr_xCuO_4$.

In the range $0.22 < x < 0.30$, we may anticipate the stabilization of charge fluctuations that segregate the superconductive phase from the overdoped metallic phase below some critical temperature not yet identified experimentally. Moreover, the appearance of a succession of superconductive phases with different vibronic modes is a possibility; such a phenomenon would clearly demonstrate the vibronic character of the superconductive phase.

Independent evidence for the condensation of a polaron gas to a polaron liquid, i.e., from uncoupled to coupled polarons, on cooling through $T_l$ in the range $0.10 \leq x \leq 0.22$ comes from recent $^{63}$Cu $1/T_1$ data obtained with nuclear quadrupole resonance.[49] At temperatures $T > T_l$ (their $T^*$ corresponds to $T_l$ in Fig. 1), the nearest-neighbor exchange interaction is almost independent of doping; the nuclear spin-lattice relaxation rate $1/T_1$ is dominated by short-range order, and the data indicate that the holes doped into the $CuO_2$ sheets do not change significantly the short-range order, which is precisely what is predicted with a polaron model. On the other hand, on cooling through $T_l$ the *d*-electron spins were found to undergo a crossover to a more itinerant regime. A correlation polaron, whether formed by spin-spin exchange or by electron-phonon interactions, would be "dressed" in antiferromagnetic spin fluctuations associated with hole-poor regions. The fact that the $^{63}$Cu $1/T_1$ data exhibit a magnetic-field dependence only for $x \leq 0.04$ suggests to us that the driving force for coupling the polarons lies primarily in the electron-phonon interactions; but the spin fluctuations should nevertheless reflect the localized *versus* itinerant character of any vibronic states.

We therefore conclude that below $T_l$ in the range $0.10 \leq x \leq 0.22$ condensation of the correlation polarons into a polaron liquid leads to extended vibronic states with a dispersion relation like that shown in Fig. 3(c). Coupling of the polarons forces us to look for an appropriate extended wave having the translational symmetry of the crystal. The logical choice, which preserves the coexistence of ionic and covalent Cu-O bonding, would be vibronic extended states representing an electron state coupled to a phonon state. However, retention of identifiable polarons coupled to one another implies linear combinations of several vibronic states near $\mathbf{k}_F$, which means in turn a significant flattening of the dispersion curve near $E_F$. In addition, identifiable polarons would restore the molecular feature of a finite splitting at the half-band position of bonding and antibonding Cu-O-Cu states. Note that the vibronic states have a narrower dispersion than that calculated for a Fermi liquid. Importantly, with the collapse of $U_{\text{eff}}$ for the extended vibronic states, this model gives a well-defined Fermi surface with a locus predicted by FLT. On the other hand, a gap at the half-band position allows for a continuation of *p*-type conduction; *n*-type conduction is only established where the polaron density is too high to sustain polaron formation. With the suppression of the polarons, the system transforms to an *n*-type metal at temperatures $T < T_l$ as indicated in Fig. 3(d). Finally, the hole-poor regions separating the coupled polarons contain ionic Cu-O bonds, and so strongly correlated states associated with these regions give some spectral weight at the center positions of the original UHB and LHB in Fig. 3(c); these states vanish at the higher $x$ of Fig. 3(d).

This model allows for a coexistence of covalent and ionic Cu-O bonds of different equilibrium Cu-O bond lengths, and it permits an orderly evolution of the relative concentrations of each type; see Fig. 4. It accounts for a vibronic stabilization of a thermodynamically distinguishable phase at temperatures $T < T_l$ in which *p*-type conductivity is compatible with a Fermi surface in the locus predicted by band theory, and it provides a natural explanation for the persistence of spin fluctuations into the superconductive compositions. Moreover, it provides a basis for a quantitative discussion of the transport properties. For example, the flatness of the dispersion curve near $E_F$, which can be seen in the ARPES data,[3-5] introduces to the dispersion curve a form near $E_F$ characteristic of a giant mass in the framework of band theory. The consequence should be a breakdown even in the polaron-liquid state of the Boltzmann transport theory; it may also account for the observed broadening of the photoelectron peaks near $E_F$ in the ARPES data.

In this paper, we make no attempt to identify the attractive forces responsible for the stabilization of vibronic Cooper pairs below $T_c$. However, we note that the model contains the two features we used to construct a correlation-bag model of superconductivity, viz., strong electron-phonon coupling and a collapse of the parameter $U$ on going from a region of ionic bonding to one of covalent bonding.[50]

In closing, it is useful to compare with Fig. 3 the evolution with $x$ in $La_{2-x}Sr_xCuO_4$ of the room-temperature ($T < T_l$) optical conductivity $\sigma(\omega)$ as measured by Uchida *et al.*[38] (Fig. 5). First, the 2.0 eV gap found for $La_2CuO_4$ remains, but with a spectral weight that decreases with increasing $x$ throughout the range $0 \leq x < 0.10$. A mid-IR peak at 0.5 eV appears immediately with doping; in Fig. 3(b), it corresponds to excitation of an electron from the LHB to the polaron hole. In

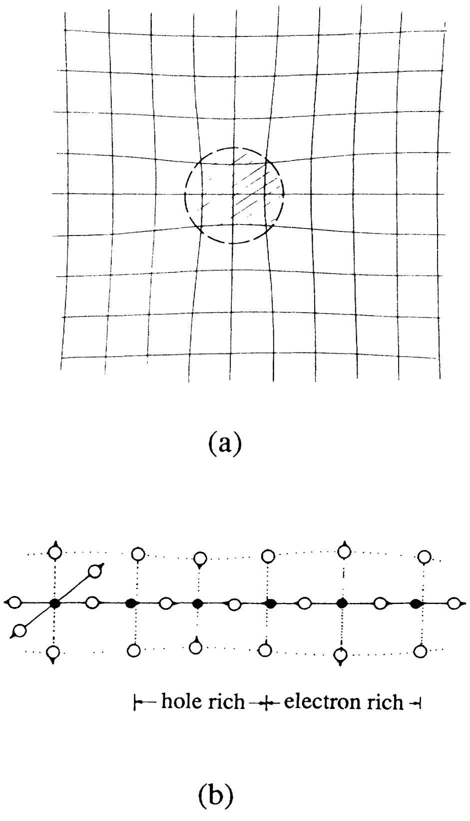

FIG. 4. Schematic representation of MO Cu-O bonding (shaded area) coexisting with ionic Cu-O bonding: (a) individual polaron moving within antiferromagnetic spin fluctuations and (b) a vibronic wave of coupled polarons for large **k**.

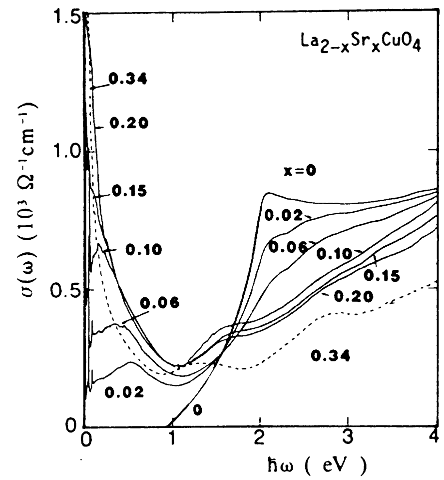

FIG. 5. Optical conductivity $\sigma(\omega)$ obtained from the Kramers-Kronig transformation of the $E \perp c$-axis reflectivity spectra for various compositions $x$ of single-crystal $La_{2-x}Sr_xCuO_4$ as presented by Ref. 38.

the range $0.10 \leq x \leq 0.22$, three new features appear: (a) a Drude component signaling the appearance of a continuous range of electronic states across $E_F$, (b) a lower intensity charge-transfer gap shifted to 1.5 eV, and (c) the appearance of a second mid-IR peak near 0.2 eV that increases relative to the 0.5 eV peak as $x$ increases. The Drude component signals the introduction of extended states, the extended vibronic states in Figs. 3(c) and 3(d). The new charge-transfer gap represents charge transfer from occupied extended vibronic states with relatively large density near $E_F$ to the UHB, and the 0.2 eV mid-IR peak could be due to charge transfer across the energy gap in the vibronic dispersion curve of Fig. 3(c). Timusk, Porter, and Tanner[11] have argued from their $\sigma(\omega)$ data on the $YBa_2Cu_3O_{7-\delta}$ system that the mid-IR structure appearing at 0.2–0.5 eV is due to electron-phonon interactions within a Rice-Wang[51] "charged-phonon" mechanism. This deduction is compatible with the model presented here. Bozovic[52] has calculated the $\sigma(\omega)$ to be expected for a polaron gas by means of classical mechanics and obtained a mid-IR peak. Mihailovíc *et al.*[53] have analyzed the frequency dependence of the photoinduced infrared conductivity $\sigma_p(\omega)$ and compared it with $\sigma(\omega)$ for several copper oxide superconductors. A concurrent shift in energy of both $\sigma_p(\omega)$ and $\sigma(\omega)$ from system to system has led them to conclude that the origin of the mid-IR feature is the same for both dilute and concentrated limits and that the charge carriers in the normal state of the high-$T_c$ cuprates are polarons or bipolarons. In our model, we keep the polaronic features necessary to retain the mid-IR peak on condensation of a polaron gas to a polaron liquid, but the model also allows for the introduction of a Drude term as well as the continuous shift in peak frequency with doping that is observed. This evolution with doping is not accounted for by a simple gas of noninteracting polarons or bipolarons.

In summary, we have defined a correlation polaron of intermediate size that nevertheless moves diffusively, but without a motional enthalpy, where the interpolaron interactions are weak. This polaron is distinguished from the conventional large polaron. In addition, where the correlation-polaron concentration is large enough for strong polaron-polaron interaction, we have postulated a condensation from a polaron gas to a polaron liquid having a dispersion relation with a flat $\epsilon_{\mathbf{k}}$ versus $\mathbf{k}$ curve near $E_F$ and a gap at the half-band position. This model allows interpretation of several seemingly contradictory properties of the high-$T_c$ copper oxides, including (1) a large Fermi surface for the optimally doped and overdoped samples that does not change with a change from $p$-type to $n$-type conduction, (2) a phase segregation below 300 K to an antiferromagnetic and a superconductive phase in the underdoped region and, it would appear,[54] between a superconductive and a metallic phase in the overdoped region, (3) a segregation of the superconductive phase below 950 °C in $La_{2-x}Ba_xCuO_4$ into two nonsuperconductive phases, (4) a temperature variation of the Seebeak coefficient that indicates a large statistical contribution in the underdoped samples and, in the optimally doped samples, a change to a strongly mass-enhanced transport term at temperatures $T < T_l$, and (5) the appearance of excess spectral weight in the energy gap of the parent antiferromagnetic phase on doping.

A strong electron-phonon interaction is built into a collapse of the Hubbard U within our correlation polaron, and stabilization of extended vibronic states in the polaron-liquid phase leaves some spectral weight in the Hubbard bands that is associated with ionic Cu-O bonding between the covalently bonded regions. Thus the polaron liquid represents a quite unique physical state, and the condensation of Cooper pairs from such a state therefore makes high-$T_c$ superconductivity a distinguishable physical phenomenon. The characteristic frequency of the polaron liquid is no longer a Debye frequency, as in conventional superconductors; we have suggested a characteristic energy of the form $\hbar\omega = (E_F \Delta U)^{1/2}$, where $\Delta U$ is the change in the Hubbard $U$ on passing from an ionic to a covalent region of Cu-O bonding.[50]

## ACKNOWLEDGMENTS

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