Thermoelectric power in single-layer copper oxides

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The temperature variation of the thermoelectric power has been measured and used as a diagnostic tool to determine the character of the charge carriers in the normal state of the superconductive copper oxides and in the overdoped compositions. We used copper oxides with single CuO2 sheets separated by nonsuperconductive layers that are not charge reservoirs in order to simplify interpretation of the data. Both the superconductive and the overdoped samples are characterized by a "hump" in the variation of the Seebeck coefficient α with temperature T that is superposed on a weakly temperature-dependent background term α_0 that decreases systematically with increased doping in the superconductive phase to a small, doping-independent value in the overdoped samples. Perturbation of the periodic potential in the CuO_2 sheets and increasing the separation between the sheets suppresses both the hump in α versus T and superconductivity. The maximum in the hump occurs at $T_{\text{max}} \approx 140 \text{ K}$, which requires a characteristic energy for any enhancement mechanism that is higher than can be provided by acoustic phonons. It is difficult for theoretical models of the normal state that are based only on electron-electron and/or conventional electron-phonon interactions to explain these data. However, we can interpret the hump with a mass-enhancement phenomenon that utilizes vibronic coupling of electrons to optical-mode lattice vibrations. From a first-principles analysis of the thermopower data, we distinguish two closely related types of the itinerant-particle state: one is applicable to the normal state of the copper-oxide superconductor compositions in the temperature range $T_c < T < 300$ K and the other to the overdoped phase.

INTRODUCTION

At the present time there is no consensus on the character of the normal state of the high- T_c copper oxides. To address this problem, we have undertaken measurements of the thermoelectric power versus temperature for several single-layer copper oxides at the optimum doping concentration and we have extended our earlier measurements¹ of the temperature dependence of the Seebeck versus temperature the coefficient in La_{2-x}Sr_xCuO₄ to include the transition from optimally doped to overdoped samples, $0.15 \le x \le 0.30$; the earlier study addressed the underdoped to optimally doped range $0 \le x \le 0.15$. We have chosen copper oxides with single CuO₂ sheets between nonsuperconductive layers that are not charge reservoirs for two reasons: (1) they allow a study of the evolution of properties as the interlayer spacing is changed or the coordination of the copper in the CuO₂ sheets is perturbed so as to suppress superconductivity at optimum doping and (2) they avoid any contribution to the Seebeck coefficient from "charge reservoirs" in the nonsuperconductive intergrowth layers.

Our lack of understanding of the normal state of the superconductive ${\rm CuO_2}$ sheets has been highlighted by attempts to interpret the transport properties. For example, a resistivity $\rho \sim T$ extends to highest temperatures T without saturation on approaching the mobility limit imposed by the Boltzmann transport theorem; the Hall coefficient R_H is temperature dependent to high T and its scaling temperature is outside the Debye temperature range; the temperature dependence of the Seebeck coefficient, α versus T, shows a broad maximum below room temperature that can be characterized by a hump

superposed on a weakly temperature-dependent background to give a maximum $\sim\!15~\mu\mathrm{V/K}$ added contribution to the background α at $T_{\rm max}\!\approx\!140~{\rm K.}^1$ The hump in the α versus T curve cannot be accounted for easily by either phonon drag or the mass-enhancement mechanism found in metals and alloys. These discrepancies combined with the fact that the isotope effect is near zero for optimally doped samples have reinforced our awareness of the breakdown of a Fermi-liquid model that is supplemented by electron-phonon interactions describable within the Migdal perturbative approximation.

In this paper, we point out that models based only on electron-electron, including magnetic, interactions and/or on conventional electron-phonon interactions have difficulty accounting for the transport data. With an alternate starting point,4 we have proposed a model based on the observation of a crossover from "ionic" Cu-O bonding in the parent antiferromagnetic phase to covalent bonding in the overdoped metallic phase and on evidence of a double-well potential at such a crossover, which can lead to a vibronic valence-fluctuation resonance. The model begins with the definition of a new type of large polaron, a correlation polaron, that moves with zero motional enthalpy and has a size of the order of 4-6 Cu atoms and their coordinating oxygen atoms. Inside such a polaron, vibronic valence fluctuations suppress the on-site electrostatic (correlation) energy Uresponsible for stabilizing localized spins at the Cu atoms in the ionically bonded region outside the polaron. At higher temperatures $T > T_l$, the polarons of a superconductive composition form a polaron gas; at $T_c < T < T_l$ the polarons condense into a polaron liquid, which represents a distinguishable thermodynamic state. The

high- T_c superconductive state is condensed from such a polaron-liquid normal state; at higher doping, the polaron concentration is too high to sustain the polaron liquid, but the valence fluctuations persist to give an anomalous overdoped metallic phase.

Several significant theoretical advances have recently been made that support such a starting point. Yonemitsu, Bishop, and Lorenzana⁵ have shown that modulation of the overlap integral in a Cu-O bond by bondlength vibration can suppress the magnetic moment on the Cu atoms as postulated for the interior of a correlation polaron; Kresin and Wolf⁶ have argued that the isotope effect in the optimally doped composition may be near zero provided the Cu-O bond potential is either anharmonic or has a double well; Ishihara, Egami, and Tachiki⁷ have demonstrated that at the crossover from ionic to covalent bonding the electron-phonon interactions are too strong to be treatable in a perturbation approximation, which is also the case where a vibronic state is stable; and Emin⁸ has developed his large bipolaron theory to argue that a bipolaron liquid can be stabilized at a doping density intermediate between that for a large bipolaron gas and that for a metallic state, an argument that should also apply to large correlation polarons.

EXPERIMENT

Samples of $La_{2-x}Sr_xCuO_4$, $(La_{1-x}Nd_x)_{1.85}Sr_{0.15}CuO_4$, and $La_{0.85}Sr_{1.15}GaCuO_5$ were prepared from the corresponding oxides and $SrCO_3$ by standard ceramic techniques. The $La_{2-x}Sr_xCuO_4$ system was annealed at 900 °C in oxygen for one month, the other samples for 2-3 days. The oxygen stoichiometry of the products was determined by iodometric titration. The oxygen content of samples $La_{2-x}Sr_xCuO_4$, $0.15 \le x \le 0.30$, were all 3.99 ± 0.01 per formula unit. The lattice parameters evolved monotonically with x and there were no impurity phases present in any of our samples to room-

temperature x-ray diffraction. The existence of a solid solution at room temperature over the entire range $0 \le x \le 0.30$ has been carefully monitored by precise scanning of several x-ray diffraction peaks and curve fitting to Lorentzian peaks. The temperature dependences of the resistances for ceramic samples of this system have been published;9 the data were comparable to published single-crystal data. Quenching in air from 1210°C reduced the oxygen content for $La_{1.65}Sr_{0.35}CuO_{4-\delta}$ to $4-\delta=3.9$. On increasing x in $(La_{1-x}Nd_x)_{1.85}Sr_{0.15}CuO_{4-\delta}$, the small oxygen deficiency δ increased; a slight oxygen deficiency (4.98 \pm 0.01) was also found in La_{0.85}Sr_{1.15}CuGaO₅. All samples were single phase to x-ray powder diffraction. The Seebeck coefficient and high-temperature conductivity were measured with homemade apparatus that has been described elsewhere. A correction for the contribution from the Cu leads was made to measurements of the Seebeck coefficient.

RESULTS

Figure 1 shows the temperature dependences of the Seebeck coefficients in the range 20 < T < 300 K for the optimally doped superconductor La_{1.85}Sr_{0.15}CuO₄ and an oxygen-deficient nonsuperconductive composition La_{1.65}Sr_{0.35}CuO_{3.90}. The two curves of Fig. 1 are plotted together for comparison because they have the same number of holes per Cu atom in their CuO2 sheets. Comparison with single-crystal data 10 has shown that α measured on polycrystalline samples corresponds to the contribution from the CuO2 sheets. We assume that the oxygen vacancies in La_{1.65}Sr_{0.35}CuO_{3.90} are located at the apical-oxygen sites, see insert Fig. 1. The vacancies suppress the superconductivity to be expected for 0.15 holes per Cu atom in the lower x^2-y^2 Hubbard band of the CuO₂ sheets. Suppression of the superconductivity

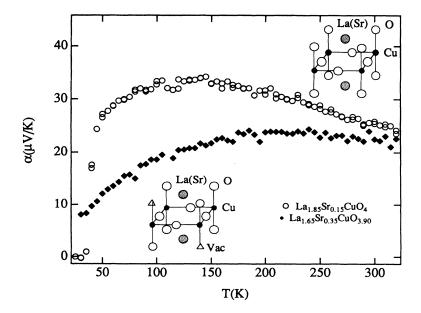


FIG. 1. Seebeck coefficient α versus temperature T for two samples with the same oxidation state of the CuO_2 sheets in the $La_{2-x}Sr_xCuO_{4-\delta}$ system. Inserts show oxygen vacancies introduced at apical sites for $La_{1.65}Sr_{0.35}CuO_{3.9}$.

occurs universally where Cu atoms of the same ${\rm CuO_2}$ sheet have different oxygen coordination, which perturbs the periodic potential in a sheet. Resistance measurements down to 10 K showed the sample to be semiconductive.

Above room temperature, each sample of Fig. 1 has an $\alpha \approx 20 \mu V/K$ that is weakly temperature dependent. This behavior could be characteristic of a polaron gas, which has its Seebeck coefficient dominated by a statistical contribution that depends only on the hole concentration; the hole concentrations in the CuO₂ sheets are the same in the two samples. The two curves of Fig. 1 diverge below room temperature; the superconductive phase has an added contribution $\delta \alpha$ to α , i.e., $\alpha = \alpha_0 + \delta \alpha$, that gives a broad maximum in α versus T at $T_{\text{max}} \approx 140$ K. The added contribution, which corresponds to the difference between the two curves, has the form of a "hump;" it is characteristic of the normal-state Seebeck data of all copper-oxide superconductors in a temperature interval $T_c < T < T_l$, where $T_l \approx 300$ K, provided there is no contribution to α from nonsuperconductive layers. This observation demonstrates that the added hump arises from a change in the character of the mobile holes below T_l in the normal state of the superconductive CuO₂ sheets and that this change requires a periodic potential and itinerant states in these sheets. We have suggested that the change is due to condensation of the polaron gas present at $T > T_l$ into a polaron liquid at $T < T_l$;⁴ this condensation introduces a dispersion of the momenta of one-quasiparticle states.

Figure 2 shows the influence of substituting Nd for La on the α versus T curve of superconductive $(\text{La}_{1-x}\text{Nd}_x)_{1.85}\text{Sr}_{0.15}\text{CuO}_{4-\delta},\ 0 \le x \le 0.08$. The single-phase T/O structure is maintained over this compositional range, but some small $(\delta \approx 0.02)$ oxygen deficiency was observed for x > 0. The concentration of oxygen vacancies was not large enough to suppress T_c , but it did

systematically reduce the concentration of holes in the ${\rm CuO}_2$ sheets with increasing x. This decrease manifests itself in the weakly temperature-dependent background; it increases with x. The shape and magnitude of the added hump remains essentially unchanged even though perturbation of the periodic Cu-atom potential from the oxygen vacancies lowers T_c .

Figure 3 shows the variation of α with T for the composition $\text{La}_{0.85}\text{Sr}_{1.15}\text{CuGaO}_5$, which again contains single CuO_2 sheets that are doped to 0.15 hole per Cu atom in the lower x^2-y^2 Hubbard band. Resistance measurements showed the sample to be semiconductive over the measuring range $10 \le T \le 300$ K. The width of the nonsuperconductive layer is increased by the insertion, between rocksalt (001) planes, of a GaO layer in which the oxygen vacancies are ordered so as to give corner-shared GaO_4 tetrahedra, 11 see insert of Fig. 3. This phase is activated in its conductivity and is not superconductive; the hump in the α versus T curve is missing.

Figure 4 shows the influence on α versus T of overdoping the system La_{2-x}Sr_xCuO₄ over the range $0.15 \le x \le 0.30$. Significantly, the weakly temperaturedependent background to α decreases systematically with increased hole doping through the superconductive compositions $0.15 \le x \le 0.26$, but it becomes small and doping independent in the overdoped phase. Nevertheless the added $\delta \alpha$ hump contribution with a $T_{\text{max}} \approx 140 \text{ K}$ is retained although the magnitude of the contribution at $T_{\rm max}$ is reduced. The anomalous metallic properties in the overdoped samples clearly retain the peculiar characteristic of the normal state of the superconductive samples that is responsible for the added hump in the α versus T curves. This observation prompts a reexamination of the evolution with x of the temperature dependence of the resistance R over the compositional range $0.15 \le x \le 0.3$.

The temperature dependence of our high-temperature

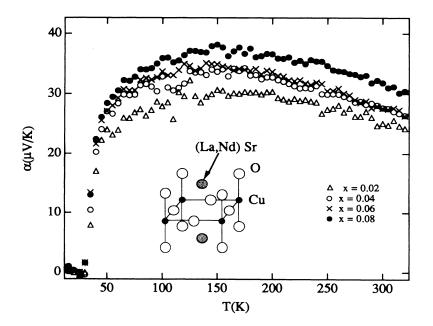


FIG. 2. Seebeck coefficient α versus temperature T for $(La_{1-x}Nd_x)_{1.85}Sr_{0.15}CuO_{4-\delta}$.

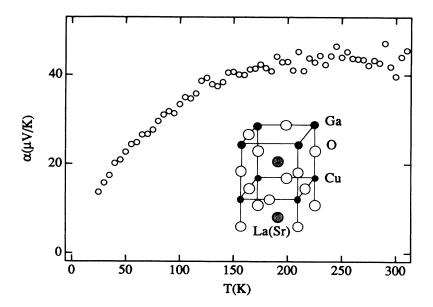


FIG. 3. Seebeck coefficient α versus temperature T for La_{0.85}Sr_{1.15}GaCuO_{5- δ}.

measurements of resistance R for $\text{La}_{2-x} \text{Sr}_x \text{CuO}_4$, $0.15 \le x \le 0.3$, exhibited two distinguishable temperature domains; R increased linearly with T in the interval $T_c < T < T_u$; for $T > T_u$, it could be fit to the formula $R = a_0 + a_1 T^y$ with $1.0 < y \le 1.2$ increasing with x. Figure 5 shows four typical R versus T curves, normalized to room temperature between room temperature and 550 °C. In sample x = 0.15, a perfect linear temperature dependence is found to an upper-limit temperature $T_u = 350$ °C. The temperature T_u decreases with increasing x to 250 °C at x = 0.19; it falls to about 150 °C for x = 0.2, see Fig. 6, but the interval $T_c < T < T_u$ remains finite for all superconductive samples. Figure 6 also shows that y increases monotonically with x to a maximum near x = 0.27, the doping limit beyond which the sharp transition in resis-

tance at T_c and any significant Meissner fraction disappear; a $T_u > T_c$ cannot be identified at x = 0.27, and α does not evolve further with increasing x.

Low-temperature resistance and Seebeck data for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ have already been published. Comparison of our value of y with that given by Takagi et al. for the overdoped samples shows a discrepancy arising from the analysis of the data. Whereas Takagi et al. used the entire temperature range $T > T_c$ to fit their data to a $\rho = a_0 + a_1 T^n$ dependence, we restrict ourselves to T > 300 K because at lower temperatures an $n \approx 2$ is found. If the entire temperature range is included, our $p \approx 1.2$ would be increased to $p \approx 1.5$ as reported by Takagi et al.

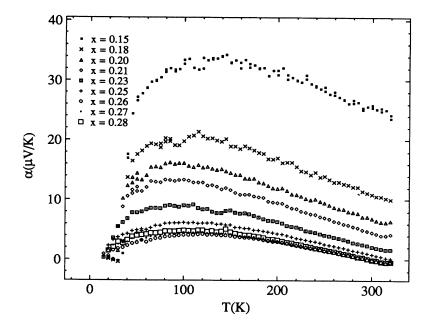


FIG. 4. Seebeck coefficient α versus temperature T for the system $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, $0.15 \le x \le 0.28$.

DISCUSSION

In an optimally doped CuO₂ sheet, the normal state below room temperature can be classified as consisting of itinerant charge carriers: it exhibits a well-defined Fermi surface, a low and only weakly temperature-dependent magnetic susceptibility, and metallic conduction. Itinerancy is conventionally described within the framework of Fermi-liquid theory and the Boltzmann adiabatic approximation for the electron-phonon interactions. We first show that this framework is unable to account for our data or those of other experiments selected from the literature. We consider electronic interactions with acoustic phonons as well as the various electron-electron interactions that have been proposed. Next we turn to valence fluctuations, which depend on fluctuations in the Cu:3d-O:2p hybridization in the Cu-O bonds; we show that within the framework of a mass-enhancement phenomenon, vibronic coupling to optical-mode lattice vibrations can give a characteristic energy that is high enough to account for the $\delta \alpha$ hump with a $T_{\text{max}} \approx 140$ K. The mass-enhancement mechanism depends on the details of the dispersion curves near the Fermi energy ϵ_F as also does the magnitude of the background contribution α_0 to α . We show that valence fluctuations can account for the hump in α and that the data distinguish different dispersion curves for the superconductive and the overdoped compositions. The dispersion curve for the superconductive samples contains an unusual gap at the midband position that can be accounted for if the normal state is a polaron liquid; the gap disappears in the overdoped compositions.

Fermi liquid

In Fermi-liquid theory, the electrons and phonons of a solid are treated adiabatically. Bands of itinerant one-electron or quasiparticle states are constructed for a static array of atoms and electron-phonon interactions are introduced via perturbation theory or the Boltzmann model in order to account for the observed transport proper-

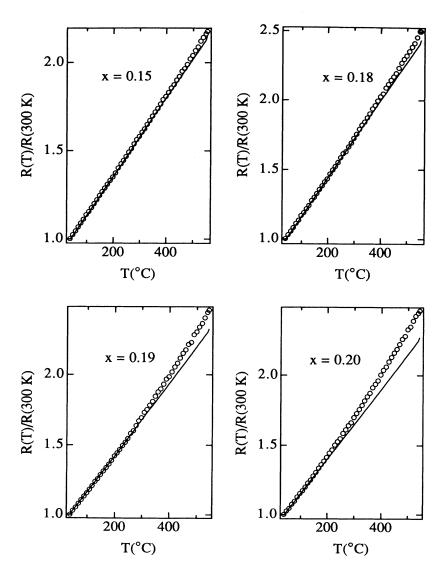


FIG. 5. Temperature dependence of resistance normalized to the resistance at room temperature R (300 K) for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, x=0.15, 0.18, 0.19, 0.20.

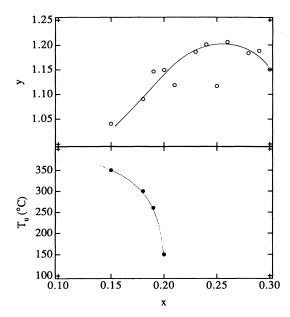


FIG. 6. The compositional dependence of the parameters T_u and y of the expression $R(T) = a_0 + a_1 T^y$ applicable for $T > T_u$. The lines are guides to the eye.

ties. Under these conditions and at not too low a temperature, the Seebeck coefficient for a metal is given by Mott's formula

$$\alpha = -\frac{\pi^2 k}{3e} k T \frac{\partial \ln \sigma(\epsilon)}{\partial \epsilon} \big|_{\epsilon = \epsilon_F} , \qquad (1)$$

where $\sigma(\epsilon) = f(\epsilon)[1-f(\epsilon)]g(\epsilon)\mu(\epsilon)$ is the product of the density of one-particle states $g(\epsilon)$, $\mu(\epsilon)$ is the particle mobility at an energy ϵ relative to a band edge, and $f(\epsilon)$ is the Fermi distribution function. The formula is applicable where there is no singularity or abrupt change in the density of states near ϵ_F . At low temperatures it is necessary to add to this transport term another due to either "phonon drag" or a "mass enhancement" arising from impurity scattering.

Phonon drag

Phonon drag appears at temperatures low enough that phonon-phonon interactions are negligible, but high enough for the density of phonon states to be important. Collisions between phonons reduce the "drag" of electrons by the phonons in a temperature gradient. At higher phonon concentrations, phonon-phonon collisions cause the phonon-drag component of α to fall off as T^{-1} ; and according to the Debye law for the specific heat, the number of phonons available at low temperatures to drag the electrons varies as T^3 . These temperature dependences result in an additional contribution $\delta\alpha$ to the Seebeck coefficient having a temperature dependence in the form of a hump with a $T_{\rm max}$ at about 20% to 30% of the Debye temperature. Although the phonon drag $\delta\alpha$ gives a hump of the appropriate shape, this mechanism is not applicable to the high- T_c copper oxides for several reasons. First, a $T_{\rm max} \approx 140$ K is significantly higher than

20% of the Debye temperature. Moreover, Johnson and Mahan¹³ have shown that the phonon-drag addition $\delta \alpha$ is small relative to Mott's term of Eq. (1) with $\delta\alpha/\alpha_0 \sim T$ only at low temperature; a $\delta\alpha/\alpha_0 \sim T^{-2}$ above $T_{\rm max}$ makes the correction negligible by room temperature. ^{11,12} Second, a Mott $\alpha_0 \sim T$ dependence is not observed at any temperature T < 800 K in the $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ superconductor.1 Third, free phonons or a phonon gas is required for phonon drag, and Allen et al. 14 have argued from their thermal-conductivity data that a phonon-gas model is not applicable to the high- T_c copper-oxide superconductors. Fourthly, MacDonald 12 has pointed out that the sign of the phonon-drag correction depends on the nature of the electron-phonon interactions that produce it; normal electron-phonon interactions contribute a $\delta \alpha < 0$ whereas Umklapp processes give a $\delta \alpha > 0$. In the p-type copper-oxide superconductors, the hump is in a positive direction $(\delta \alpha > 0)$, in the *n*-type superconductors it is in a negative direction $(\delta \alpha < 0)$; the hump in the superconductive oxides always adds to the magnitude of α . There is no evidence to suggest that the electron-phonon processes are different in the n-type superconductors from

those in the p-type superconductors.

Cohn et al. 16 have argued for a phonon-drag model in YBa₂Cu₃O₇₋₈, but this material contains contributions from the Cu-O chains as well as the CuO2 sheets. In their latest report on a twin-free crystal, 17 the chain contribution was derived to be positive. However, with $\delta = 0.04$ and approximately 0.20 holes/Cu(2) in the CuO₂ sheets, the valence of the chain copper Cu(1) is formally 2.52+, which corresponds to a y^2-z^2 conduction band that is less than half-filled. We should therefore expect to find a negative contribution to the Seebeck coefficient. The Seebeck coefficients of doubly doped YBa₂Cu₃O_{7-δ} indeed show that the contribution to α from the Cu-O chains is negative. 18 The origin of the positive contribution found by Cohn et al. 17 remains unidentified; failure to subtract properly the negative contribution from the Cu-O chains puts into question the curve fitting used to argue for a phonon-drag model.

Mass enhancement

A mass-enhancement contribution has been identified in metal alloys where a short phonon mean free path makes inapplicable a phonon-drag model. ¹⁹ In this model, a nonperiodic potential provides a strong scattering of the electrons near the Fermi surface; this scattering modifies the one-electron dispersion curve near the Fermi energy ϵ_F so as to enhance the mass of the charge carriers with energy near ϵ_F . In this case, the Seebeck coefficient can be written as ²⁰

$$\alpha = \alpha_0 [1 + a\lambda\lambda_s(T)], \qquad (2)$$

where α_0 is Mott's transport term, a is a constant, $\lambda = g(\epsilon_F)V$ is the electron-phonon coupling constant, and

$$\lambda_{s} = \frac{\int d\epsilon \beta^{2} F(\epsilon) G_{s}(\epsilon/kT)/\epsilon}{\int d\epsilon \beta^{2} F(\epsilon)/\epsilon}$$
(3)

is the normalized mass-enhancement factor. In Eq. (3), $G_s(\epsilon/kT)$ is a universal function²⁰ and $\beta^2 F(\epsilon)$ is the Eliashberg function.

This model and a similar one based on an electronphonon-impurity interference,²¹ like the phonon-drag model, gives a supplemental hump term having a T_{max} about 20% of the Debye or Einstein temperature. In all these models, T_{max} is limited by the fact that the electrons are interacting with acoustic phonons, which are excited at low temperature. For most metals and alloys, these mechanisms give a hump with a $T_{\rm max} \le 20$ K. ^{12,22} Available phonon data for the copper oxides give a maximum energy of the acoustic-phonon modes at a Debye temperature $\theta_D \approx 100 \text{ K}$, although Junod²⁴ has given a $\theta_D \approx 400$ K for the system $\text{La}_{2-x} \text{Sr}_x \text{CuO}_4$. From these estimates of θ_D , a $T_{\text{max}} \approx 0.2\theta_D \le 80$ K is predicted for models based on electron interactions with acoustic phonons. This upper limit is well below the $T_{\text{max}} \approx 140 \text{ K}$ observed experimentally as illustrated in Fig. 1. The result would seen to implicate a mechanism that modifies the one-particle dispersion curve near ϵ_F as does the universal function $G_s(\epsilon/kT)$ of Eq. (3), but with a characteristic energy given by the optical rather than the acoustic branch of the phonon spectrum. The choice of an electron interaction with an optical-mode lattice vibration is not only indicated by a $T_{\text{max}} \approx 140 \text{ K}$, it is also dictated if we are to introduce valence fluctuations associated with vibronic states stabilized by strong electron coupling to a resonance between ionic and covalent equilibrium Cu-O bond lengths.

Figure 1 provides a test of the effect of a vacancy or defect on the thermopower of optimally doped CuO₂ sheets. In La_{1.65}Sr_{0.35}CuO_{3.90}, the oxygen vacancies reduce the oxidation state of the CuO₂ sheets to that of La_{1.85}Sr_{0.15}CuO₄, but they also perturb the periodic potential at the Cu atoms. According to the model of mass enhancement by impurity scattering, scattering from the vacancies should enhance the hump in the α versus T curve; but just the opposite effect is observed, see Fig. 1. Similarly, La_{0.85}Sr_{1.15}GaCuO₅ has optimum doping of the CuO₂ sheets and is not superconductive; it too exhibits an α versus T curve that has no hump. In these samples, a large α_0 is indicative of polaronic conductivity, but the lack of a $\delta \alpha$ hump in α versus T is similar to what is found in underdoped samples. The polaron gas of the underdoped samples has no dispersion of one-particle energies; we conclude that development of a dispersion curve and of a well-defined Fermi surface are necessary conditions for both superconductivity and the anomalous hump in the α versus T curve. In La_{1.65}Sr_{0.35}CuO_{3.90}, perturbation of the periodic potential suppresses the development of a dispersion curve. In La_{0.85}Sr_{1.15}GaCuO₅, it is not clear whether it is the larger separation, from 13 to 16 Å, of the CuO₂ sheets or a perturbation of the periodic potential that suppresses formation of the dispersion curve.

Although the existence of a dispersion curve, a Fermi surface, and a vibronic mass enhancement appear to be necessary conditions for high- T_c superconductivity, the persistence of the $\delta\alpha$ hump into the overdoped composi-

tions shows they are not sufficient conditions. We postulated the formation of a polaron liquid in the superconductive compositions in order to introduce a dispersion of the one-particle energies;4 in the overdoped region, polaron formation is inhibited by too large a concentration of charge carriers. A polaron liquid introduces two features missing from the overdoped compositions: first a midband energy gap that reflects the gap between bonding and antibonding states within the individual polarons and, second, retention of an interface between domains of vibronic and ionic Cu-O bonding. Across the interface, there is a discontinuity ΔU in the on-site electrostatic Coulomb energy. A discontinuity in the correlation energy ΔU and the existence of a dispersion curve are the two essential conditions for a "correlation-bag" model of superconductive-pair formation.

Electron-electron interactions

Alternatively, attempts have been made to account for the hump with purely electron-electron interactions. For example, the marginal-Fermi-liquid theory gives an α that increases with decreasing temperature, 25 but the authors were forced to attribute the downturn of α below $T_{\rm max}$ to superconductive-pair fluctuations. Such an assumption may be reasonable enough where the superconductive layers contain multiple CuO2 sheets with a $T_c \approx 100$ K, but it is clearly incorrect in $La_{2-x}Sr_xCuO_4$ where $T_c \approx 40$ K and a $T_{\text{max}} \approx 140$ K are observed. Moreover, the resistance anomaly attributable to the onset of superconductive-pair fluctuations, about 46 K, falls well below T_{max} ; there is no resistive anomaly near T_{max} . In addition, Fig. 4 demonstrates that the hump contribution in the La_{2-x}Sr_xCuO₄ system extends into the compositional range where there is no superconductivity, which would seem to rule out the pair-fluctuation hypothesis and to cast doubt on the marginal-Fermi liquid as a viable candidate to describe the copper-oxide prob-

In other purely electronic models, including the spinfluctuation, spin-bag, and resonant-valence-bond (RVB) models, the characteristic energy that replaces the Debye energy is a low-lying magnetic excitation. It is important to test this hypothesis experimentally. An early experiment²⁶ indicated that α is independent of magnetic fields up to 30 T, but the data were taken at only three fixed temperatures. We²⁷ have measured α as a function of magnetic field from 0 to 8 T over a temperature range 70 < T < 300 K in $La_{2-x}Sr_xCuO_4$. Over this range of magnetic field, there is no change in the α versus T curves. We also substituted some Nd for La to introduce an additional internal molecular field; but no change in the hump was observed, see Fig. 3. These experiments cast doubt on magnetic models that utilize magnetic excitations as a characteristic energy.

To provide further evidence that magnetic excitations are not relevant to the mechanism responsible for the anomalous hump in α versus T in the superconductive copper oxides, we return to Fig. 4. In the overdoped samples, the spin fluctuations are suppressed; yet the hump persists with the same $T_{\rm max} \approx 140~{\rm K}$. Therefore we

conclude that the characteristic energy of the mechanism responsible for the hump in α , and probably also for T_c , is not magnetic in origin.

VALENCE FLUCTUATIONS

In a transition-metal oxide, a valence fluctuation can be said to occur where there is a fluctuation between two states each with a different covalent component in the M-O bonds. Such a fluctuation requires the existence of a double well in the electronic potential versus M-O bond length. A double-well potential separating "ionic" from covalent M-O bonding has been found in the LNiO3 compounds (L = rare earth).²⁸ In this context, ionic bonding occurs where the empty 3d energies are far enough above the valence-band edge that covalent mixing of O-2p and M-3d orbitals can be treated in second-order perturbation theory; the resulting crystal-field orbitals may then be localized or itinerant depending on the strength of any metal-metal or metal-oxygen-metal interactions. In a covalent model, the covalent mixing is treated in first-order theory. The more ionic M-O bond length is longer than the covalent bond length; kinetic energy is sacrificed in order to gain a greater potential energy in the more ionic

It has been recognized for some time²⁹ that a special feature of the superconductive copper-oxide systems is a crossover from more ionic to covalent bonding on oxidation of the parent antiferromagnetic sheets. In the parent compounds, the x^2-y^2 band of the CuO₂ sheets is split by on-site Coulomb energies into an empty upper Hubband band separated by 2 eV from the top of the O-2p bands and a lower Hubbard band that is filled and, in an ionic model, lies below the top of the O-2p bands. Therefore oxidation of the CuO2 sheets introduces holes that cannot occupy an ionic bond (they are not located in ionic O-2p bands); they occupy orbitals in which the Cu-3d and O-2p hybridization must be treated in first-order theory. Even in metallic LaCuO₃, which contains Cu(III) with a half-filled σ^* band, an important 3d component in the band generates a mass enhancement of the magnetic susceptibility.³⁰ In La_{2-x}Sr_xCuO₄, the magnetic susceptibility also shows a temperature dependence extending into the overdoped compositions that signals the presence of an important Cu-3d component in the partially filled $x^2 - y^2$ band.³¹

Oxidation of the CuO_2 sheets with increasing x in $La_{2-x}Sr_xCuO_4$ introduces a mixed-valent situation in which ionic and covalent bonding must coexist if there is no phase segregation. Coupling of the holes to an optical-mode lattice vibration may introduce a resonance between the two types of bonding rather than a static or quasistatic spatial resolution of the two bond types as occurs in a charge-density wave or a small polaron. Such a resonance would correspond to a valence fluctuation.

Electronic specific heat provides important evidence for the presence of valence fluctuations in the superconductor and overdoped compositions.³² The γ coefficient is near zero in the parent compound and remains small in the underdoped compositions. It increases with x>0.1 to a maximum of about 9 mJ/mol K^2 at x=0.15 and

essentially saturates on further increase of x into the overdoped compositions. This behavior is to be contrasted with that of $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$ where γ becomes huge at the boundary of the metal-insulator transition, but drops dramatically with further doping into the metallic phase.³³

In our high-temperature resistance measurements, data above T_u fit to a power law. This power-law behavior is expected in a heavy Fermion or strongly correlated electron system. However, the linear relation between R and T below T_u indicates that, in addition to valence fluctuations, some other phenomenon is also present in the normal state of the superconductive phase.

Newns and co-workers³⁴ and more recently Brandow³⁵ have developed a valence-fluctuation model to describe the high- T_c superconductors. Brandow, in particular, has pointed out that a valence-fluctuation state is thermodynamically distinguishable from the antiferromagnetic parent state; the material should undergo a first-order transition on passing from one to the other. This prediction is in accord with the observation of a phase segregation in the La₂CuO_{4+δ} system³⁶ and of evidence for a dynamic phase segregation below 150 K in La_{2-x}Sr_xCuO₄. ¹ However, we will argue that the overdoped region is described by the valence-fluctuation model; the superconductive phase contains valence fluctuations within polarons formed at $T < T_u$, but the normal state has in addition, the form of a polaron liquid at temperatures $T_c < T < T_1$

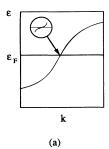
Valence fluctuations and thermoelectric power

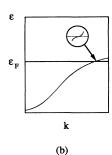
In the discussion of the Seebeck coefficient, we were able to rule out mechanisms capable of producing a $\delta\alpha$ hump with a $T_{\rm max}\approx 140$ K if the characteristic energy depended on coupling to acoustic phonons. Where there are valence fluctuations, there is an important coupling to optical-mode vibrations; the characteristic energies for optical-mode vibrations are high enough to yield a $T_{\rm max}\approx 140$ K. Since we were able to rule out purely electronic mechanisms, an interaction with optical-mode vibrations becomes a compelling possibility.

We begin with the observation that the magnitude of α decreases with increasing x in the superconductive phase, but not in the overdoped phase, whereas the added hump in α versus T persists into the superconductive phase. In order to clarify the situation, we start with a more general formula for the Seebeck coefficient³⁷

$$\alpha = -\frac{k}{e} \int d\epsilon \frac{(\epsilon - \epsilon_F)}{kT} \cdot \frac{\sigma(\epsilon)}{\sigma} , \qquad (4)$$

where $\sigma(\epsilon)$ is the same as in Eq. (1) and $\sigma = \int d\epsilon \, \sigma(\epsilon)$ is the total conductivity. From this expression, it is apparent that at a fixed temperature T the magnitude of α is a measure of the imbalance in the contributions from electrons above and below the Fermi energy ϵ_F . For metals, α is clearly a minimum where the Fermi energy is at an inflection point in the ϵ versus k dispersion curve as pictured in Fig. 7(a); it is at a maximum where the curvature at ϵ_F is largest as in Fig. 7(b). Expression (4) does





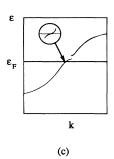


FIG. 7. Schematic dispersion curves for (a) a conventional metal, (b) a conventional metal with a small Fermi surface, and (c) a p-type polaron liquid all with mass enhancement (see inserts).

not include the correction term $\delta\alpha$ due to the interaction of the charge carrier with another medium such as the phonons. Without losing generally, another term must be added to Eq. (4), which gives

$$\alpha = -\frac{k}{e} \int d\epsilon \frac{\left[\epsilon - \epsilon_F + D(\epsilon, T)\right]}{kT} \cdot \frac{\sigma(\epsilon)}{\sigma} \ . \tag{5}$$

From this expression, we draw two conclusions: first, the magnitude of α for a given temperature is determined primarily by the details of the dispersion curve in the vicinity of ϵ_F and, second, an interaction between the charge carrier and some other medium will change the shape of the ϵ vs k curves near ϵ_F as a function of temperature so as to give a hump in the α versus T curve with a $T_{\rm max}$ defined by a characteristic energy of the interaction as in the case of phonon drag of mass enhancement.

We may deduce from these two general conclusions and the data of Fig. 4 that the optimally doped superconductive phase has a dispersion curve with an important imbalance across ϵ_F as shown in Fig. 7(b). Normally this situation can only occur near the top of a band, which would mean a small Fermi surface. However, photoemission, 38 conductivity, 2 and positron-annihilation 39 experiments, among others, indicate that the Fermi surface is large and located a little below the half-band filling position predicted by band calculations⁴⁰ with no correlation energy (U=0). Moreover, a mid-IR excitation⁴¹ locates a gap somewhere near ϵ_F . This situation leads to a dispersion curve for the superconductor phase like that of Fig. 7(c), but with a midband gap that is not opened up by the translational symmetry of the crystal. This is precisely the model we have discussed elsewhere⁴ for the dispersion curve of a correlation-polaron liquid. For x > 0.26, the magnitude of α is small and does not change with doping, which indicates that in these samples ϵ_F is located in a position of the dispersion curve like that of Fig. 7(a). This deduction means that the midband energy gap has disappeared as would be predicted for a transition from the polaron-liquid phase to a phase of homogeneous charge density of the copper atoms. Since the molecular orbitals inside a correlation polaron were defined as vibronic in character, the transition to a phase with homogeneous charge density may retain the vibronic character of the electron-phonon coupling. In fact, we have cited the variation with doping in the electronicspecific-heat parameter γ and power law in the hightemperature resistance in support of valence fluctuations in the overdoped samples. Interactions with the optical phonons modify the dispersion curve so as to increase the effective mass; these modifications are reflected in the mass-enhancement factor of Eq. (3), but with a characteristic energy that raises $T_{\rm max}$ from that of the conventional mass-enhancement factor. Significantly, these modifications do not create the imbalance in curvature on either side of ϵ_F that is needed to raise α_0 , so α_0 falls to a small value with the closing of the midband energy gap whereas $\delta\alpha$ remains unaffected so long as vibronic coupling is retained.

Spectral weight and thermoelectric power

Three important features of the Seebeck coefficients of the copper-oxide superconductors have been noted: (1) the large magnitude of α_0 , (2) a dependence of α_0 on doping that is not present in the overdoped samples, and (3) a $\delta\alpha$ hump in the α versus T curve that persists into the overdoped compositions. We now make a more fundamental analysis of these three features.

For a system in which all the charge carriers are involved in transport, as in a polaronic system, the Fermi energy ϵ_F of Eq. (4) represents a chemical potential μ_0 . In this case, solution of Eq. (4) with a purely statistical term at high enough temperature leads to the Heikes formula; the contribution from a residual transport term is much smaller. The statistical term gives an important dependence on the effective occupancy number of the partially filled state. In contrast, this doping dependence is not applicable to conventional itinerant-electron systems with a well-developed dispersion of the one-particle energies; in this case, only the charge carriers near ϵ_F participate in charge transport, Fig. 8(a). As a result, conventional itinerant-electron systems are described by Mott's formula, Eq. (1), and α depends on doping only through the density of one-particle states $g(\epsilon)$ at ϵ_F . We observe, Fig. 4, such an insensitivity to doping in the overdoped compositions, but not in the superconductive samples even though the superconductors exhibit an itinerant-particle character in the temperature range $T_c < T < T_l$. This observation signals an important distinction between the normal state of the superconductive phase at temperatures $T < T_u$ and the overdoped compositions. On the other hand, a $\delta \alpha$ hump with a $T_{\text{max}} \approx 140$ K in both the superconductive and the overdoped compositions signals that, though distinguishable, these two compositional ranges have a common feature that distinguishes them both from conventional metals. We have

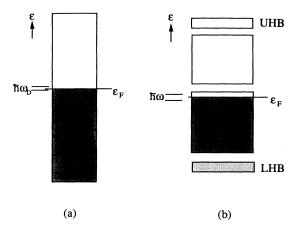


FIG. 8. Schematic energy diagram for (a) a conventional metal showing the small fraction of states lying in the energy range $\hbar\omega_D$ and (b) a polaron liquid showing the fraction of states lying in the energy range $\hbar\omega$, where ω is an optical-mode frequency.

argued above that the common feature can be accommodated in a charge-fluctuation model in which the mobile holes occupy itinerant vibronic states formed by a strong coupling of the mobile holes to optical phonons. We consider now what feature can distinguish the normal state of the superconductors from the overdoped samples.

In a previous paper,4 we pointed out that if the holes introduced into the CuO2 sheets by doping form large correlation polarons, then spectral weight is transferred from the upper and lower Hubbard bands to the energy gap between them; this spectral weight is associated with the vibronic molecular orbitals formed within each polaron. Moreover, for x > 0.1 and $T < T_l$, we postulated a condensation of the gas of correlation polarons into a polaron liquid. Strong coupling between polarons in the polaron-liquid state organizes the states transferred from the Hubbard bands into the gap so that they exhibit a narrow band of itinerant-particle states having k as a good quantum number, while retaining an energy gap at the midband position; the gap reflects the bonding and antibonding character of the vibronic molecular orbitals inside each polaron. Because ionic and vibronic Cu-O bonding continue to coexist in the polaron liquid, residual states corresponding to the ionic Cu-O bonds remain in the positions of the upper and lower Hubbard bands, see Fig. 8(b). So long as the original Hubbard x^2-y^2 bands retain ionic-bond states, additional doping can bring new states into the energy domain near ϵ_F ; α_0 remains doping dependent because the number of states near ϵ_F changes with doping via spectral-weight transfer. With this model, which represents a unique way to interpret the doping dependence of α_0 only in the underdoped and superconductive compositions, the superconductive phase is distinguished from the underdoped polaron gas compositions by the formation of itinerant states in a polaron liquid and it is distinguished from the overdoped compositions by retention of states in the upper and lower Hubbard bands that are associated with the residual ionic Cu-O bonding in the polaron-liquid state. In addition,

the superconductive compositions are distinguished from the overdoped compositions by retention of a midband energy gap that also disappears with the states in the two Hubbard bands in the transition to the overdoped phase. It is only at temperatures $T > T_u$ that the superconductive and overdoped phases become indistinguishable.

Nomenclature

Coupling of electronic and vibrational modes of the same symmetry introduces vibronic states having both electronic and vibrational character. In a crystal, the electronic and vibrational states that mix may have an itinerant character that senses the translational symmetry of the crystal; the particles that occupy these states may be labeled vibrons to distinguish them from Fermions on the one hand and polarons on the other. Alternatively, the vibronic states may be restricted to a more local range as in the correlation polaron that we have described elsewhere.4 Condensation of a gas of correlation polarons into a polaronic liquid retains the polaron character and is therefore to be distinguished from a state composed of a homogeneous distribution of vibrons even though both states exhibit a dispersion of one-particle energies in momentum space. The polaron liquid represents an inhomogeneous distribution of charge density; it is characteristic of the normal state of the superconductive phase. The overdoped phase has a homogeneous distribution of charge as the vibrons belong equally to all like atoms of the phase. Where valence fluctuations are stablized, whether within correlation polarons or itinerant vibronic states, it is not possible to treat the electronphonon interactions within the Boltzmann adiabatic approximation or the Migdal perturbation scheme.

CONCLUSIONS

From our analysis of the transport data reported in this paper, we have been able to establish the following points:

- (1) The temperature and composition dependencies of the Seebeck coefficient of copper-oxide superconductor systems cannot be interpreted within the framework of conventional electron-phonon interactions, the marginal-Fermi-liquid theory, or any of the several magnetic models that have been proposed to describe the electronic properties of the copper-oxide superconductors.
- (2) The superconductive phase can be distinguished from the underdoped and overdoped compositions by having both a large, dopant-dependent α_0 and a $\delta\alpha$ hump; the underdoped samples share only the former property and the overdoped samples only the latter.
- (3) The presence of a hump in the α versus T curve indicates modification of a dispersion curve near ϵ_F as a result of interaction of itinerant electrons with another medium; however, we believe a $T_{\rm max} \approx 140$ K is too high to be accounted for by either "phonon drag" or a mass enhancement due to impurity scattering. On the other hand, $T_{\rm max} \approx 140$ K is compatible with an electron interaction with optical-mode phonons such as would be

encountered in a vibronic resonance between ionic and covalent Cu-O bonding.

- (4) A high, dopant-dependent value of α_0 indicates a diffusive transport with an important statistical contribution as in a polaron gas. However, in the transition from a polaron gas to an itinerant-particle state, the statistical term would lose its meaning. On the other hand, a high α_0 is retained because the midband energy gap creates a strong imbalance of the curvature on either side of ϵ_F and a dopant-dependent α_0 is retained via the Hubbard-band states associated with ionic Cu-O bonding; the Hubbard-band states coexist with a narrow-band dispersion curve associated with the polaron liquid. A high α_0 would be retained on formation of the polaron liquid because bonding and antibonding states within a polaron introduce an energy gap at the midband position, which places ϵ_F only a little below the top of the lower half-band.
- (5) The overdoped phase has no midband energy gap, which results in a smaller α_0 ; but it is an unconventional metal in which valence fluctuations are associated with vibronic states. A hump in the α versus T curve and a power law in the R versus T curve are signatures for the existence of vibronic states and a dispersion of one-

quasiparticle energies. Although vibronic states are also present in the underdoped samples, they can only give a $\delta\alpha$ hump where the one-particle states form a dispersion curve. In the underdoped samples and where superconductivity is suppressed at optimal doping, no dispersion curve is formed and there is no $\delta\alpha$ hump.

Finally, we call attention to the fact that, within the interpretation presented, the transition from superconductive to overdoped compositions is associated with a loss of boundary between domains of vibronic and ionic bonding, a boundary across which the on-site electrostatic Coulomb energy U changes discontinuously. A discontinuity ΔU across an interface and the existence of a dispersion curve are the two essential conditions for a "correlation-bag" model of high- T_c superconductivity; they are both provided by a polaron liquid and vibronic coupling within the polarons, ionic bonding without.

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