

Interlayer coupling and the thermopower of cuprate superconductors

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A review of the extant literature on the thermopower (TEP) of the cuprate superconductors reveals a transition from polaronic to homogeneous itinerant electron behavior with increasing hole concentration in the CuO_2 sheets. Superconductivity appears at the compositions of crossover from one regime to the other, and the normal state of the superconductors retains a heterogeneous electronic structure of mobile hole-rich and hole-poor domains, which introduces both a statistical and a transport component to the Seebeck coefficient. A primary manifestation of the transport component is an enhancement term $\delta\alpha(T)$ having a maximum at a $T_{\text{max}}=100\text{--}140$ K, which is characteristic of a strong coupling of the charge carriers to optical rather than acoustic phonons. Comparison of the TEP for $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ vs $\text{La}_{0.85}\text{Sr}_{1.15}\text{GaCuO}_5$ and $\text{La}_{1.8}\text{Sr}_{0.2}\text{CaCu}_2\text{O}_{6+\delta}$ vs $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ indicates that an increase in the c -axis coupling between neighboring CuO_2 sheets increases the size of the polaron or hole-rich domains in the underdoped compositions, thereby lowering the room-temperature value of the Seebeck coefficient $\alpha(300\text{ K})$ and increasing the magnitude of $\delta\alpha(T)$. These observations implicate a strong elastic component, enhanced by electron-lattice interactions, in the c -axis coupling as well as in the formation of larger nonadiabatic polarons and their interactions within the CuO_2 planes. They also signal that caution must be exercised in any application of a ‘‘universal plot’’ of $\alpha(300\text{ K})$ versus hole concentration p per Cu atom in a CuO_2 plane to obtain a value of p from TEP data. [S0163-1829(96)00842-9]

INTRODUCTION

The strong anisotropic conductivity of the high- T_c copper-oxide superconductors and the intergrowth architecture of their structures have drawn primary attention to the role of the CuO_2 sheets in the superconductive mechanism. On the other hand, coupling between the CuO_2 sheets along the c axis has also been proved to play a critical role in establishing the superconductive state. In this paper, we consider the influence of the c -axis coupling on the thermoelectric power (TEP) of this family of oxides. We also review briefly the evidence from TEP measurements for a heterogeneous electronic state in the superconductive composition, and we interpret our results in the perspective of a model for this heterogeneous state that we have previously proposed.

THERMOELECTRIC POWER

TEP measurements have proven to be a useful probe of the character of the charge carriers in solids; they give reliable information for polycrystalline as well as single-crystal samples. In general, the TEP measurements contain three contributions:

$$\alpha(T) = \alpha_s + \alpha_t(T) + \delta\alpha(T), \quad (1)$$

where α_s is a statistical term that is dominant in the case of small-polaron charge carriers, $\alpha_t(T)$ is a transport term that measures the mean curvature of the charge-carrier energy-dispersion curve $\varepsilon(k)$ at the Fermi surface, and $\delta\alpha(T)$ is a low-temperature enhancement that requires a charge-carrier energy dispersion to be manifest. The statistical term α_s , as described by Heikes’s formula, is temperature independent, but it varies strongly with the occupancy fraction of the sites over which it moves. Therefore the statistical term can be

used to measure the mean size of polaronic charge carriers having a given density. The transport term is relatively small, but it is dominant where the charge carriers are itinerant; its magnitude increases linearly with temperature in a metallic system with a fixed number of carriers. The most common low-temperature enhancement is due to phonon drag, a phenomenon reaching a maximum at a temperature $T_{\text{max}} \approx 0.2 \theta_D$, where θ_D is the Debye temperature. We shall argue that the TEP of the cuprate superconductors is dominated by the statistical term α_s , in the underdoped compositions with $p \leq 0.1$ hole carriers per Cu atom of a CuO_2 sheet and by the transport term in the overdoped samples with $p \geq 0.25$. In the superconductive compositional range $0.1 < p < 0.25$, the statistical term and transport terms both make important contributions to the TEP, which provides a clear indication that the superconductive phase is electronically heterogeneous.

DATA REVIEW

We begin with a review of several critical features of the TEP data that have been obtained for the system $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. This system has been considered to be atypical because it falls off a so-claimed¹ ‘‘universal plot’’ of room-temperature Seebeck coefficient $\alpha(300\text{ K})$ versus hole concentration p per Cu atom in the CuO_2 sheets. However, it is, in fact, one of the most straightforward and informative systems to consider as it contains no charge reservoir and therefore gives direct information on the transport properties of the CuO_2 sheets. It is the ‘‘atypical’’ behavior that introduces the issue of the c -axis coupling. In this system, single CuO_2 sheets are coupled to one another along the c axis through an insulating $\text{La}_{2-x}\text{Sr}_x\text{O}_2$ rocksalt layer, and it is possible to vary the compositional parameter x over the range $0 \leq x \leq 0.30$, while retaining oxygen stoichiometry as

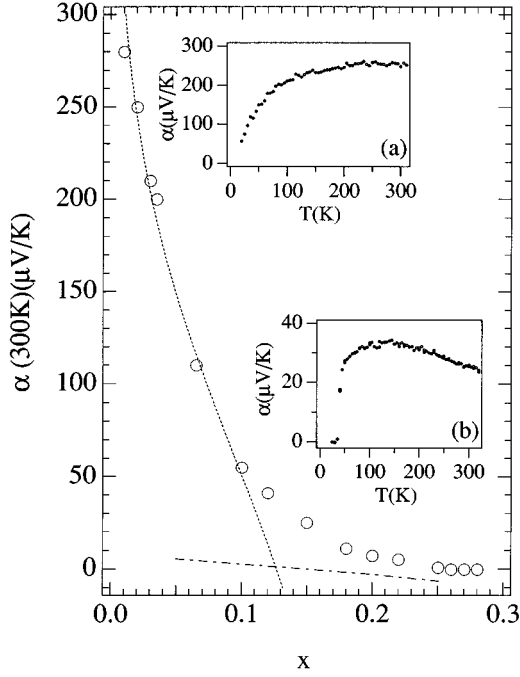


FIG. 1. The plot of TEP at room temperature $\alpha(300\text{ K})$ for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. The dashed line represents the curve fitting to a logarithmical function in the range $0 < x \leq 0.1$. The dot and dash line showing the result of a band calculation is taken from Ref. 3. Inset (a) and (b) give the temperature dependence of TEP for the samples $x=0.02$ and $x=0.15$, respectively.

has been demonstrated by Takagi *et al.*² with fine-focus synchrotron x-ray diffraction.

In the underdoped compositional range $0 < x \leq 0.1$, the TEP of the system $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is temperature independent above about 200 K. The inset (a) of Fig. 1 shows a curve of α vs T for the $x=0.02$ sample, which gives a typical behavior for this doping range. The magnitude is given by the room-temperature value, which varies as

$$\alpha(300\text{ K}) \approx (k/e) \ln[2(1 - k_1 x)/k_1 x], \quad (2)$$

where $k_1 = 5.3$ and the factor 2 in the brackets is a spin-degeneracy factor, see Fig. 1. Such a variation with hole concentration x of a temperature-independent α shows that the statistical term dominates in the TEP; it is typical of the TEP imparted by nonadiabatic polarons provided the mean size of a polaron is increased from one Cu site to 5.3 Cu sites.

In the overdoped compositions, $x > 0.25$, the Seebeck coefficient is described by the relation

$$\alpha(T) = \alpha_r(T) + \delta\alpha(T), \quad (3)$$

where $\alpha_r(T)$ is small and insensitive to doping as calculated for a band model;³ the enhancement term $\delta\alpha(T)$, which sets in below room temperature, has a maximum at $T_{\text{max}} \approx 100\text{ K}$, a temperature that is too high to be due to a conventional phonon-drag enhancement by acoustic phonons.⁴ Indeed, phonon-drag enhancements with a $T_{\text{max}} \approx 75\text{ K}$ in the metallic chains of $\text{Sr}_2\text{CuO}_{3+\delta}$ (Ref. 5) and $T_{\text{max}} \approx 65\text{ K}$ in metallic LaCuO_3 (Ref. 6) have been observed. A vibration mode giving $T_{\text{max}} \approx 100\text{ K}$ has not been recognized. In $\text{YBa}_2\text{Cu}_4\text{O}_8$,

however, an optical-mode vibration⁷ could be assigned to give rise to a $T_{\text{max}} \approx 120\text{ K}$. We therefore conclude that the overdoped compositions are electronically homogeneous, but the itinerant electrons are unusual as they couple strongly to optical phonons rather than to acoustic phonons.

In the superconductive range $0.1 < x \leq 0.25$, the Seebeck coefficient has been described⁴ by the relation

$$\alpha = \alpha_0 + \delta\alpha(T), \quad (4)$$

where $\alpha_0 \approx \alpha(300\text{ K})$ is nearly temperature independent above room temperature; it is strongly composition dependent which distinguishes it from the overdoped compositions, but it decreases more slowly than logarithmically with increasing x . The inset (b) of Fig. 1 gives the temperature dependence of α for the $x=0.15$ sample; it is typical for the superconductive compositional range. The extension of the fitting curve for the underdoped compositions falls to negative beyond $x=0.1$ instead of at $x=0.5$ as small polarons. It is interesting to note that the TEP measured in the range $0.1 < x \leq 0.25$ follows neither extrapolation of the large polaronic picture found for $0 < x \leq 0.1$ nor that of the itinerant-electron band model (dashed line). The high TEP relative to the band calculation together with the strong doping dependence indicates that the statistical term still plays a role. It therefore appears that we have

$$\alpha_0 = \alpha_s + \alpha_t(T), \quad (5)$$

where the transport contribution $\alpha_t(T)$ is relatively weak. On the other hand, the enhancement term $\delta\alpha(T)$ with a $T_{\text{max}} = 100\text{--}140\text{ K}$ in the range $0.1 < x \leq 0.25$ is much larger in the superconductive samples than in the overdoped samples. This unprecedented behavior, indicative of a coexistence of an important statistical term and a large enhancement term, signals the existence of a single crystallographic phase containing two electronic phases: one is hole-rich corresponding to a condensation of interacting polarons and the other is hole-poor supporting spin fluctuations. Emery⁸ has used other arguments to conclude that the normal state of the copper-oxide superconductors is electronically inhomogeneous. We have argued elsewhere⁹ that the heterogeneous state is formed by a condensation of the polaron gas of the underdoped composition into a polaron liquid with the possibility of the formation of a polaron solid below T_c .¹⁰ In such a condensation, the polaron-polaron interactions lifting the degeneracy give rise to a dispersion of the mobile-particle energies, which allows the manifestation of a $\delta\alpha(T)$, and causes the polarons to lose their individual identities as they interact to form hole-rich domains. Equation (2) states that, for a given hole concentration $x=p$, a decrease in $\alpha_s = \alpha(300\text{ K})$ must correspond to an increase in k_1 and hence in the mean size of the polarons in the underdoped compositions. Extrapolation of this result into the superconductive compositions having heterogeneous hole-rich and hole-poor domains would give a larger volume of the hole-rich domains for a lower $\alpha(300\text{ K})$ at a fixed value of p .

We emphasize next that superconductivity in the copper oxides has been unambiguously correlated with a TEP for the CuO_2 sheets that shows the coexistence of the enhancement $\delta\alpha(T)$ having a $T_{\text{max}} \approx 140\text{ K}$ and an α_0 that is strongly

doping dependent.⁴ For example, $\delta\alpha(T)$ is not present in the TEP of either the underdoped sample or an optimally doped $\text{La}_{1.65}\text{Sr}_{0.35}\text{CuO}_{3.90}$ in which perturbation of the periodic potential of a CuO_2 sheet by oxygen vacancies suppresses superconductivity. In this latter example, the insulating layer between CuO_2 sheets is retained as a rocksalt layer, so the c -axis coupling should be similar in the nonsuperconductive sample to that in superconductive $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, and α_0 does not change with the suppression of superconductivity. We conclude that the electronic heterogeneity was retained in $\text{La}_{1.65}\text{Sr}_{0.35}\text{CuO}_{3.90}$, but loss of the periodicity of the electronic potential suppressed the enhancement mechanism together with the superconductivity. Moreover, measurements of $\alpha(T)$ under different hydrostatic pressure P (Ref. 11) for $x=0.13, 0.15$, and 0.22 in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system gave a $dT_c/dP=0.2$ and 0.1 K/kbar for the two orthorhombic samples with $x=0.13$ and $x=0.15$, but a $dT_c/dP=0$ for the tetragonal sample with $x=0.22$. Where a $dT_c/dP>0$ occurred, pressure also increased the magnitude of the enhancement $\delta\alpha(T)$; the enhancement was independent of pressure where $dT_c/dP=0$. In addition, angle-resolved photoemission spectroscopy on other superconductive samples has demonstrated a flattening with increasing T_c of the charge-carrier dispersion $\varepsilon(\mathbf{k})$ in the direction of the Cu-O-Cu bonds in the CuO_2 plane.¹² From these experiments, we conclude that a single underlying physical phenomenon is responsible for the increase in T_c , the flattening of $\varepsilon(\mathbf{k})$ in the Cu-O-Cu bond directions, and the TEP enhancement $\delta\alpha(T)$.

These general properties described for the CuO_2 sheets in the system $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ have been found to hold also for the CuO_2 sheets in the other cuprate superconductors wherever it has been possible to eliminate contributions to the TEP from conductive layers between the CuO_2 sheets. Nevertheless, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is ‘‘atypical’’ in one respect; the magnitude of $\alpha(300\text{ K})$ for $x\geq 0.1$ remains anomalously high when compared on the ‘‘universal plot’’ of $\alpha(300\text{ K})$ vs $T_c/T_{c\text{max}}$ for a given hole concentration in the CuO_2 sheets.

Attempts to rationalize this anomaly as a manifestation of oxygen vacancies or of orthorhombic-tetragonal phase fluctuations are not tenable; the measured overdoped compositions were stoichiometric,² no detectable orthorhombic fluctuations were found down to 10 K for $x\geq 0.21$,¹³ and there is no anomaly in the TEP at the orthorhombic-tetragonal transition.⁴ Moreover, $\text{La}_2\text{CuO}_{4+\delta}$ can be doped to the optimal hole concentration ($p=0.14$ at $\delta=0.07$) by the insertion of interstitial oxygen into the middle of the La_2O_2 rocksalt layer; the TEP at $\delta=0.07$ is identical to that of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$.^{14,15} Finally, measurement of the TEP under a high magnetic field has eliminated any magnetic origin for the anomaly.¹⁶ We propose here that the higher, with respect to the ‘‘universal plot’’, $\alpha(300\text{ K})$ found for $x>0.1$ in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is caused by a weaker c -axis coupling between the CuO_2 sheets.

INFLUENCE OF THE c -AXIS COUPLING

In order to test whether c -axis coupling has any influence on the TEP, we begin with the compound $\text{La}_{0.85}\text{Sr}_{1.15}\text{GaCuO}_5$, Fig. 2(b), in which the $\text{La}_{2-x}\text{Sr}_x\text{O}_2$ layer of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ Fig. 2(a), has been replaced by a

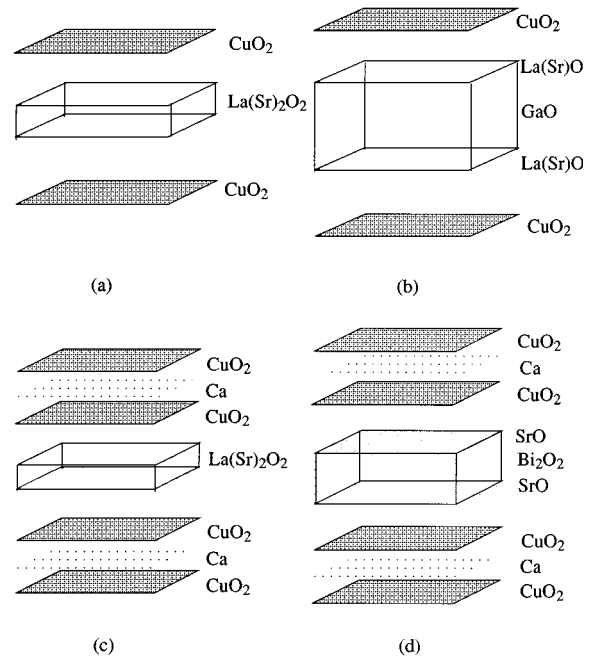


FIG. 2. Schematic drawing of the crystal structures of (a) $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, (b) $\text{La}_{0.85}\text{Sr}_{1.15}\text{GaCuO}_5$, (c) $\text{La}_{1.8}\text{Sr}_{0.2}\text{CaCu}_2\text{O}_{6-\delta}$ and (d) $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$

thicker insulating layer $\text{La}_{1-x}\text{Sr}_{1+x}\text{GaO}_3$ and the doping of the CuO_2 layer is kept nearly optimal.⁴ The introduction of a GaO plane into the middle of the rocksalt layer is charge compensated by substituting one Sr for one La. The insertion of a GaO plane increases the thickness of the insulating layer separating the CuO_2 sheets from $<13\text{ \AA}$ to $>16\text{ \AA}$. $\text{La}_{0.85}\text{Sr}_{1.15}\text{GaCuO}_5$ is a semiconductor down to 10 K and its TEP contains no enhancement term $\delta\alpha(T)$; it has an $\alpha(300\text{ K})\approx 42\text{ }\mu\text{V/K}$, which is significantly higher than the $\sim 23\text{ }\mu\text{V/K}$ obtained for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, see Table I. More precisely speaking, the detectable difference in oxygen content for these samples is 0.01 by iodometric titration; this difference cannot account for the jump in TEP. It is interesting that although $\alpha(300\text{ K})$ in $\text{La}_{0.85}\text{Sr}_{1.15}\text{GaCuO}_5$ is larger, nevertheless the charge carriers have not collapsed to single-site small polarons, which should show an $\alpha(300\text{ K})\approx 223\text{ }\mu\text{V/K}$. The mean size of the polarons has only been reduced from 5.3 to 4.2 Cu sites.

Next, we compare two compounds with double CuO_2 sheets separated by a plane of Ca^{2+} ions, viz. $\text{La}_{1.80}\text{Sr}_{0.2}\text{CaCu}_2\text{O}_{6-\delta}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$. The structure of the former compound is illustrated in Fig. 2(c); it contains the same $\text{La}_{2-x}\text{Sr}_x\text{O}_2$ rocksalt layer separating the CuO_2 -Ca- CuO_2 layers of double CuO_2 sheets as is found in

TABLE I. The TEP at room temperature and the low-temperature enhancement for four cuprates.

	$\alpha(300\text{ K})$ ($\mu\text{V/K}$)	$\delta\alpha(T)$
$\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{3.99}$	23	Strong
$\text{La}_{0.85}\text{Sr}_{1.15}\text{GaCuO}_{4.98}$	42	None
$\text{La}_{1.80}\text{Sr}_{0.2}\text{CaCu}_2\text{O}_{6-\delta}$	33	Weak
$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$	8	Strong

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ separating single CuO_2 sheets. This compound becomes superconductive with a $T_c \approx 60$ K after treatment under high oxygen pressure. The hole concentration of the superconductor is $p \approx 0.12$ per Cu atom as determined by the structural refinement,¹⁷ and the resistivity vs temperature plot¹⁸ exhibits a behavior typical of an underdoped cuprate, which supports the hole-concentration value determined structurally. Like $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, this superconductor has a room-temperature TEP $\alpha(300 \text{ K}) \approx 33 \mu\text{V/K}$,¹⁸ Table I, that is higher than the “universal plot” for $p = 0.12$; and the enhancement term $\delta\alpha(T)$ is relative weak. The structure of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ is illustrated schematically in Fig. 2(d). It contains Bi_2O_2 layers between CuO_2 -Ca- CuO_2 layers of double CuO_2 sheets. The TEP reported reveals an enhancement term $\delta\alpha(T)$ below room temperature and an $\alpha(300 \text{ K}) \approx 8 \mu\text{V/K}$,¹ Table I, that falls on the universal plot for the hole concentration $p \approx 0.12$. It is apparent that the introduction of a metallic¹⁹ or a narrow-gap semiconductive layer Bi_2O_2 between the CuO_2 -Ca- CuO_2 layers of double CuO_2 sheets has reduced significantly the measured $\alpha(300 \text{ K})$ for a given hole concentration p per Cu atom in the CuO_2 sheets. The large difference in TEP between $\text{La}_{1.80}\text{Sr}_{0.2}\text{CaCu}_2\text{O}_{6-\delta}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ does not appear to be due to the change in the transport term $\alpha_t(T)$; the change in the statistical term α_s seems to be playing the dominant role, as is discussed further below.

The 90-K superconductors with the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ structure also contain metallic chains between CuO_2 -Y- CuO_2 layers of double CuO_2 sheets, the chains acting as charge reservoirs for the CuO_2 sheets. Similarly the cuprates containing double TI-O planes have been shown to have mixed-valence TI-O layers.²⁰ Although a metallic character has not been demonstrated unambiguously for the Hg cuprates, the linear O-Hg-O bonds along the c axis²¹ appear to provide strong c -axis coupling in these compounds also. Therefore, we conclude that (1) the “universal plot” of $\alpha(300 \text{ K})$ vs p may only apply where the c -axis coupling is relatively strong, and (2) there only if the contribution to the TEP from conductive layers other than the CuO_2 sheets is not significant. With respect to the latter, the TEP measurements in $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{6.96}$, for example, show a dominant chain contribution to $\alpha(300 \text{ K})$ in $\text{YBa}_2\text{Cu}_3\text{O}_{6.96}$.²²

A variation of $\alpha(300 \text{ K})$ with the strength of the c -axis coupling has another interesting implication. If $\alpha(300 \text{ K}) \approx \alpha_0$ in the superconductive and underdoped compositions is dominated by a statistical contribution to the TEP, it should provide information about the size of the polarons responsible for the statistical term. As pointed out above, a decrease in $\alpha(300 \text{ K})$ for a given hole concentration p would signal an enlargement of the mean size of the polarons or of the hole-rich domains. From the evidence cited above for a lowering of α_0 with increased c -axis coupling between CuO_2 sheets, we conclude that increasing the c -axis coupling increases the size of the hole-rich domains; it may even increase the polaron size so as to transform a nonsuperconductive polaron system into a superconductor in which larger polarons strongly interact with one another. Finally, increasing the c -axis coupling also appears to raise the amplitude of the enhancement $\delta\alpha(T)$ at $100 \text{ K} < T_{\text{max}} \leq 140 \text{ K}$ in the superconductive compositions.

DISCUSSION

The origin of the c -axis coupling between CuO_2 sheets could be electronic and/or elastic. The fact that it is stronger where the intergrowth layer between CuO_2 sheets is metallic and weakest where it is insulating and thick shows that electron transfer between the CuO_2 sheets and the intergrowth layer between them can enhance the coupling, but the dominant mechanism may still be an elastic coupling that is enhanced by electron-phonon interactions. A $T_{\text{max}} \approx 140 \text{ K}$ for $\delta\alpha(T)$, which is compatible with an enhancement associated with strong coupling of the charge carriers to cooperative fluctuations of individual Cu-O and/or O-O bond lengths, together with an increase in the magnitude of $\delta\alpha(T)$ with increased c -axis coupling would seem to signal the presence of a strong elastic component in the interactions between CuO_2 sheets along the c axis. Moreover, a unique feature of the copper oxides, which have their e -orbital degeneracy removed by the intergrowth architecture, is the possibility of a pseudo-Jahn-Teller deformation at oxidized copper centers of the square-coplanar Cu-O bonding of a CuO_2 plane. Bending from 180° of the Cu-O-Cu bond angle of a CuO_2 sheet reduces the stability of these deformations. Pressure experiments^{23,24} have shown a $dT_c/dP > 0$ where bent bonds are straightened by pressure, but a $dT_c/dP = 0$ where the bonds are initially 180° . This observation is consistent with the hypothesis that the optical-mode lattice vibrations responsible for $\delta\alpha(T)$ are dynamic pseudo-Jahn-Teller deformations. Moreover, given the strong hybridization of Cu $3d$ and O $2p$ wave functions in the $\sigma_{x^2-y^2}^*$ conduction band, cooperative fluctuations of the O-O separations may also contribute to the enhancement $\delta\alpha(T)$. These optical-mode vibrations would, in turn, be enhanced by stronger coupling to the electronic configurations.

In an attempt to understand what factor stabilizes a larger as against a small nonadiabatic polaron, a calculation has been made¹⁰ of the size of the polaron that can be stabilized by the introduction of cooperativity of the pseudo-Jahn-Teller deformations at neighboring copper centers. The cooperativity stabilizes a nonadiabatic polaron containing 5–7 Cu centers and introduces an important elastic attractive force between the polarons that is able to overcome the Coulombic repulsion between them. The larger the amplitude of the deformations, the larger the size of the polarons and the stronger the elastic interaction between them. Such a model introduces as well, but not considered in the calculation, an important elastic component to the c -axis coupling between CuO_2 sheets. In this model, increasing the c -axis elastic coupling would enhance the amplitude of the pseudo-Jahn-Teller deformations, thereby increasing the volume of the polarons (or the hole-rich domains) and the magnitude of the TEP enhancement $\delta\alpha(T)$.

CONCLUSIONS

From these considerations, we draw the following conclusions:

(1) The TEP data reveal a crossover with increasing hole concentration from polaronic conduction in the underdoped samples to a homogeneous itinerant-electron conduction in the overdoped samples. The nonadiabatic polarons of under-

doped samples are large; they have a mean size of between 5 and 6 copper centers in a CuO_2 sheet. The itinerant electrons of overdoped samples are unusual in that they give a low-temperature enhancement $\delta\alpha(T)$ having a maximum at $T_{\text{max}}=100\text{--}140$ K, which is too high for phonon drag by acoustic phonons but is appropriate for an enhancement due to strong coupling of the charge carriers to optical phonons.

(2) The TEP for the superconductive compositions indicates the continued presence in the normal state of a heterogeneous electronic distribution of mobile hole-rich domains; however, the hole-rich polarons interact to form extended hole-rich domains and to develop a carrier-energy dispersion giving a narrow, partially filled band and a Fermi surface. The development of a carrier-energy dispersion is manifest in a low-temperature enhancement $\delta\alpha(T)$ having a $T_{\text{max}}\approx 140$ K and a larger amplitude than in the overdoped samples.

(3) The size of the larger polarons, or of the hole-rich domains, and the magnitude of $\delta\alpha(T)$ at T_{max} appear to increase with increasing strength of the *c*-axis coupling between neighboring CuO_2 sheets. Increasing the strength of

the *c*-axis coupling can transform a nonsuperconductive gas of individual polarons to a superconductive state having hole-rich and hole-poor domains and showing an enhancement $\delta\alpha(T)$ in the normal-state TEP. The essential features for realization of the high- T_c superconductive state in the copper oxides appear to be (a) a heterogeneous electronic phase containing hole-rich domains coexisting with a carrier-energy dispersion giving rise to an enhancement $\delta\alpha(T)$, and (b) a significant *c*-axis coupling.

(4) As the strength of the *c*-axis coupling increases, the magnitude of $\alpha(300\text{ K})$ decreases for a given hole concentration p , at least for $p < 0.15$. Therefore the application of a claimed ‘‘universal plot’’ of $\alpha(300\text{ K})$ vs hole concentration p per Cu atom of the CuO_2 sheets to estimate the hole concentration p from a measurement of $\alpha(300\text{ K})$ must be applied with caution.

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