

**RENORMALIZED PHONON FREQUENCIES AND  
ELECTRIC RESISTIVITY ALONG THE  $c$ -AXIS  
IN SINGLE-PLANE HIGH-TEMPERATURE  
SUPERCONDUCTORS: A DOUBLE-WELL  
ANALYSIS**

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**Abstract.** We consider the dynamic interlayer charge transfer across apex oxygens between  $\text{CuO}_2$  planes in single-layered high- $T_c$  superconductors. Phonon-coupled axial transfer rates are derived by means of the reaction-rate method. They lead straightforwardly to temperature dependences for the axial resistivity. Doping and temperature dependences are also derived for the renormalized frequencies of phonon modes coupled to the interlayer charge transfer. Our results are compared with experimentally observed dependences.

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## 1. Introduction

There are two prerequisites for the occurrence of a super-conductivity: (i) pairing and (ii) long-range phase coherence. While both are understood in conventional materials, they are enigmatic in high-temperature superconductors (HTSC). (ii) requires an interlayer coupling and, indeed, a long-standing HTSC problem is the coupling of conducting  $\text{CuO}_2$  planes.

In-plane holes appear mostly in  $b_1$  linear combinations of oxygen  $2p_{x,y}$  orbitals which hybridize with copper  $3d(x^2 - y^2)$  orbitals to give rise to the main conduction band. A small amount occupies the  $a_1$  linear combination which hybridize with copper  $3d(3z^2 - r^2)$  orbitals to incite a satellite conduction band. These  $3d(3z^2 - r^2)$  copper orbitals split in energy from the copper  $3d(x^2 - y^2)$  orbitals as a result of a Jahn-Teller distortion of the  $\text{CuO}_6$  octahedron in which the apical  $\text{Cu(P)}-\text{O(A)}$  bond is elongated with respect to the in-plane  $\text{Cu(P)}-\text{O(P)}$  bond. This  $\varepsilon-\theta$  splitting, expected to give rise to Jahn-Teller polarons, has stimulated the search for a high- $T_c$  superconductivity [1].  $a_1$ -ligand holes hybridize with apex oxygen  $2p_z$  orbitals giving rise to an axial charge leak which provides part of the interplane coupling. This  $3d_{z^2} - 2p_z$  leak is really a dynamic charge transfer (CT) because it is mode-coupled [2].

In particular, coupling to the  $A_{2u}$  phonon modes in the tetragonal phase of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  has been suggested. The odd-mode coupling splits the apex oxygen sites thereby leading to the formation of broken-symmetry small polarons and bipolarons [3] or mediating carrier pairing by virtue of highly polarizable apical oxygens  $\text{O(A)}$  [4]. Temperature and doping dependent phonon frequencies possibly renormalized through coupling to electronic CT have been measured but not understood well so far, since no simple solutions have been offered to analyze experiments.

The present paper is aimed at extending the  $3d_{z^2} - 2p_z$  CT model so as to derive temperature and doping dependences for the coupled axial phonon frequencies and electric resistivities. We have considered early the free energy of a system of nonlinear vibronic oscillators with dipolar interactions and derived temperature dependences. Doping dependences are introduced assuming that the Jahn-Teller distortion of  $\text{CuO}_6$  octahedra is suppressed when occupied by extra holes. Our predictions are compared with recent experimental data [5-7].

## 2. Hamiltonian

We separate a pseudo-Jahn-Teller (pJT) part of the overall Hamiltonian to describe the observed apex-site splitting along the  $c$ -axis:

$$H_{\text{pJT}} = t_{pd}\Sigma_n(a_{pn}^+a_{dn} + a_{dn}^+a_{pn}) + (\varepsilon_{pd}/2)\Sigma_n(a_{pn}^+a_{pn} - a_{dn}^+a_{dn}) + \hbar\Omega\Sigma_n b_n^+b_n + G_{\text{pJT}}(\hbar/2NMk)^{1/2}\Sigma_n(a_{pn}^+a_{dn} + a_{dn}^+a_{pn})(b_n^+ + b_n)$$

where the subscripts  $p$  and  $d$  stand for the  $2p_z$  and  $3d_{z^2}$  orbitals, respectively,  $n$  labels the  $\text{CuO}_6$  octahedra.  $t_{pd}$  is the hopping energy,  $\varepsilon_{pd}$  is the  $2p_z^-$  to  $3d_{z^2}^-$  energy level gap,  $\Omega$  is the bare  $A_{2u}$ -mode frequency and  $G_{pJT}$  is the electron-mode coupling constant.  $a_{ni}^+$  ( $a_{ni}$ ) for  $i = d, p$  are the creation (annihilation) operators for hole carriers upon the respective orbitals. The energy reference level is set in between  $\varepsilon_d$  and  $\varepsilon_p$  and we introduce  $\varepsilon_{pd} = |\varepsilon_d - \varepsilon_p|$ . The electron-phonon mixing term is of the band off-diagonal type concomitant with the experimental evidence for site-splitting double-well potentials sensed by apex oxygens in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  [8]. Double-well potentials are generated by  $H_{pJT}$  for  $4\varepsilon_{JT} > \varepsilon_{pd}$  ( $\varepsilon_{JT} = G_{pJT}^2/2K$  is the Jahn-Teller energy where  $K$  is the stiffness). This is a strong-coupling case in which  $H_{pJT}$  creates off-center apical polarons constituting a nondegenerate gas of fermionic excitations. The average kinetic energy of a nondegenerate fermionic gas being  $k_B T$ , it explains why the Fermi energy  $\varepsilon_F$  would not appear in the resulting equations, as it would for the Fermi gas in metals. Other equations familiar from double-well physics are reproduced too [3, 4]. Missing details can be found in the references.

Separating the  $c$ -axis system from the  $a, b$ -plane is justified for a weak axis-to-plane coupling which seems to be the case in view of the observed asymmetry of the hopping energies ( $t_{\text{axial}} \ll t_{\text{planar}}$ ) and electrical resistivities ( $\rho_{\text{axial}} \gg \rho_{\text{planar}}$ ). In concomitance with shared views, the  $H_{pJT}$  physics is that of axial polarons scattered by the double wells [9].

### 3. CT Energy Gap

We first consider the electronic Hamiltonian in the absence of phonons and electron-phonon interactions. In a purely ionic picture, the CT gap is given by  $\varepsilon_{dp}$ . However, due to partial covalent bonding set forth through  $t_{dp}$ , the first two terms of  $H_{pJT}$  diagonalize in a basis by the eigenstates of the triatomic  $\text{O(A)-Cu(P)-O(A)}$  molecule with eigenvalue spectrum

$$\begin{aligned}\varepsilon_{\text{AB-NB}} &= \frac{1}{2} \left( \varepsilon_{dp} + \sqrt{\varepsilon_{dp}^2 + 8t_{dp}^2} \right) \\ \varepsilon_{\text{NB}} &\equiv \varepsilon_p \\ \varepsilon_{\text{NB-B}} &= \frac{1}{2} \left( \varepsilon_{dp} - \sqrt{\varepsilon_{dp}^2 + 8t_{dp}^2} \right)\end{aligned}$$

corresponding to the antibonding (AB), nonbonding (NB) and bonding (B) levels in their decreasing order [4]. Two new gaps  $\varepsilon_{\text{gap}}$  appear associated with the molecular energy spectrum: the splitting  $\varepsilon_{\text{B-NB}}$  between the bonding and nonbonding levels and the splitting  $\varepsilon_{\text{NB-AB}}$  between the nonbonding and antibonding levels. At  $t_{dp} \approx 0$  the upper gap is nearly ionic:  $\varepsilon_{\text{NB-AB}} \approx \varepsilon_{dp}$ , while the lower one vanishes:  $\varepsilon_{\text{B-NB}} \approx 0$ .

#### 4. Electron Hopping Along $c$ -Axis

We shall now concentrate on the electron hopping from the O(A)  $2p_z$  orbital to the Cu(P)  $d_{z^2}$  orbital. This transfer cannot occur spontaneously due to the finite energy gap  $\Delta_{CT} = |\varepsilon_d - \varepsilon_p| \approx \varepsilon_{dp}$  and requires an external stimulation, such as an optical intergap excitation. Nevertheless, the electron transfer in a non-degenerate electronic system may be promoted by its energy levels coupling to an appropriate phonon mode  $Q$ . The phonon coupling brings the two electronic energies close enough to incite an electron transfer through interlevel tunneling.

We consider the coupling of a O(A<sub>2</sub>)-Cu(P)-O(A<sub>1</sub>) molecule to the A<sub>2u</sub> axial phonon mode in tetragonal symmetry. These displacements will swing the oxygen  $2p_z$  energies from values close to the copper  $3d_{z^2}$  energy to values characteristic of an isolated oxygen. During half of a vibrational period, e. g. O(A<sub>1</sub>) comes closer to Cu(P) as O(A<sub>2</sub>) moves away. Electron tunneling may occur from  $2p_z$  to  $3d_{z^2}$  for the O(A<sub>1</sub>)-Cu(P) pair during a half-period, as it may for O(A<sub>2</sub>)-Cu(P) during the subsequent half-period. We refer to the molecular configuration at which  $\varepsilon_d(Q) \approx \varepsilon_p(Q)$  as the “crossover configuration”  $Q = Q_c$ .

Due to the odd parity of the bond-stretching A<sub>2u</sub> mode, there always is an apex oxygen O(A<sub>1,2</sub>) approaching Cu(P) as the other one moves away. Unlike A<sub>2u</sub>, both apex oxygens O(A<sub>1</sub>) and O(A<sub>2</sub>) in the “even parity” A<sub>1g</sub> breathing mode either approach Cu(P) during a vibrational half-period or go away from it altogether during the next half period. We see that the A<sub>1g</sub> motion fails to secure any O(A) at a tunneling distance from Cu(P) during the ‘goaway’ part, even though supplying two tunneling oxygen partners to the copper during the ‘goto’ part. In as much as there is no more than one electron tunneling from copper to oxygen at a time, we believe that the A<sub>2u</sub> coupling is more efficient than the A<sub>1g</sub> coupling in promoting the hole leak along the  $c$ -axis.

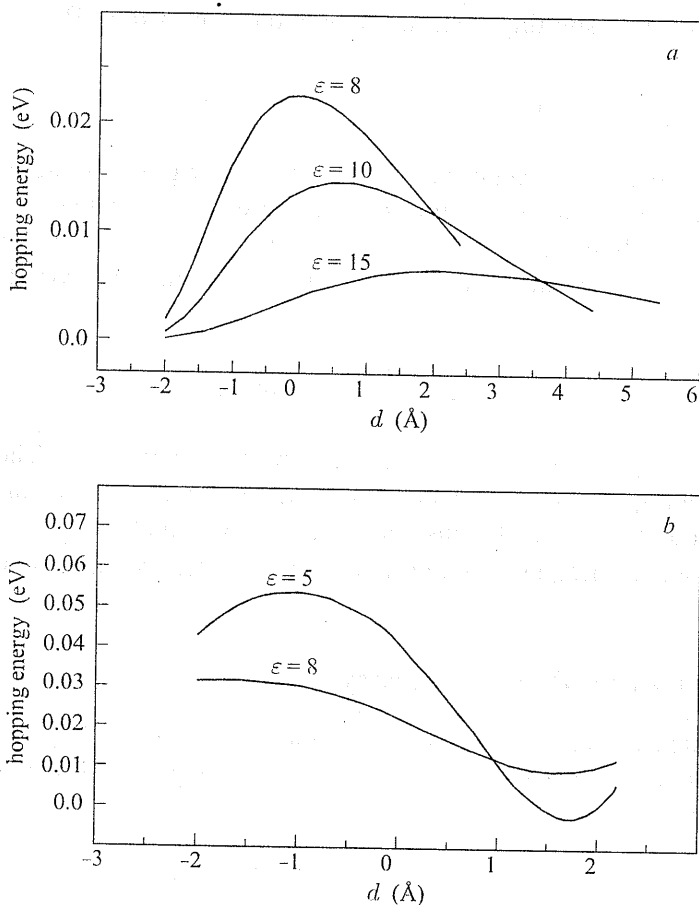
Once nearly degenerate, the O(A) and Cu(P) levels split by  $2\delta t$  due to the tunneling interaction.  $t_{dp} \equiv \delta t$  is the hopping integral of a Cu(P)-O(A) pair. The tunneling splitting is defined by  $\delta t \sim \langle 3d_{z^2} | V(r) | 2p_z \rangle$ .

We calculate  $\delta t$  by inserting the electronic potential  $V(r)$  and the wave functions into the integral. We use oxygen orbitals  $|2p_{z'}\rangle$  and  $|2p_{z''}\rangle$  and a copper orbital  $|3d_{z^2}\rangle$  in a medium with dielectric constant  $\varepsilon$ , wherein the coordinate notations for our specific geometry read:  $r' = \sqrt{x^2 + y^2 + (z - R)^2}$ ,  $z' = z - R$ ,  $r'' = \sqrt{x^2 + y^2 + (z + R)^2}$ ,  $z'' = z + R$ ,  $r = (x^2 + y^2 + z^2)^{1/2}$ . We calculate the O<sup>2-</sup>-Cu<sup>3+</sup> → O<sup>1-</sup>-Cu<sup>2+</sup> hopping energy in an electron-deficient O<sup>2-</sup>-Cu<sup>2+</sup>-O<sup>2-</sup> triatomic molecule whose eigenstates are described by hydrogen-like wave functions. We place the copper ion of charge  $Z_{Cu} = 3$  at the origin and the two oxygens of charges  $Z'_O = -1$  and  $Z''_O = -2$  at  $\pm R$  along the  $z$ -axis,

respectively, to compute the off-diagonal Coulomb energy of an electron at  $r$

$$\delta t = -\frac{1}{2} \frac{e^2}{\epsilon} \langle 3d_{z^2} | \left( \frac{Z'_O}{r'} + \frac{Z''_O}{r''} + \frac{Z_{Cu}}{r} \right) (|2p_{z'}\rangle + |2p_{z''}\rangle) .$$

Numerical results for the electron hopping integral  $\delta t \equiv t_{pd}$  are presented in Fig. 1 for two ways of modulating the O(A)-Cu(P) bond length  $R$ , as in the  $A_{1g}$  vibrational mode (a) and in the  $A_{2u}$  vibrational mode (b).



**Fig. 1.** Dependence of the electron hopping energy  $t_{dp}$  on the apex oxygen displacements  $d$  relative to the equilibrium bond lengths in the O(A)-Cu(P)-O(A) triatomic molecule  
(a)  $A_{1g}$  displacement mode; (b)  $A_{2u}$  displacement mode. Both dependences are examples for a nonlocal electron-phonon coupling

## 5. Dynamic Hopping Band

At finite  $t_{pd}$ , the ionic gap  $\varepsilon_{pd}$  is replaced by the hybridized gap  $\varepsilon_{\text{gap}}$ , while the vibronic double-well potentials turn to [4]

$$\varepsilon_{\pm}(Q) = \frac{1}{2} \left( KQ^2 \pm \sqrt{(2G_{pJT}Q)^2 + \varepsilon_{\text{gap}}^2} \right).$$

Now, due to the mode coupling, the CT hopping energy  $\delta t$  transforms into a ‘vibronic tunneling splitting’, viz. a CT polaron band width [3]

$$t_{\text{CT}} = \langle \varphi(Q + Q_0) | H | \varphi(Q - Q_0) \rangle$$

where  $\varphi(Q)$  are the renormalized harmonic-oscillator ground-state wave functions. If the Gaussian exponentials therein are approximated for by delta-functions which holds good for  $4\varepsilon_{\text{JT}} \gg \varepsilon_{\text{gap}}$  ( $\mu \equiv \varepsilon_{\text{gap}}/4\varepsilon_{\text{JT}} \ll 1$ ), one derives an expression for the range where CT is carried by small polarons [3]

$$t_{\text{CT}} \approx \frac{1}{2} \varepsilon_{\text{gap}} \exp\left(-2 \frac{\varepsilon_{\text{JT}}}{\hbar\Omega_{\text{ren}}}\right).$$

At  $\mu \approx 1$  ( $\varepsilon_{\text{gap}} \leq 4\varepsilon_{\text{JT}}$ ),  $t_{\text{CT}} \approx \frac{1}{2} \varepsilon_{\text{gap}}$ : CT is by large polarons.\* The interwell energy barrier  $\varepsilon_{\text{B}} = \varepsilon_{\text{JT}}(1 - \mu)^2 = \varepsilon_{\text{JT}}(1 - \varepsilon_{\text{gap}}/4\varepsilon_{\text{JT}})^2$  is now low and in order to have a bound state the obvious condition has to be met:  $\frac{1}{2} \hbar\Omega_{\text{ren}} \leq \varepsilon_{\text{B}}$  where  $\Omega_{\text{ren}}$  is the phonon frequency renormalized by the electron-mode coupling.

## 6. Renormalized Mode Frequency

In the isolated center limit, the bare vibrational frequency  $\Omega_{\text{bare}}$  of a vibronic oscillator is renormalized by the electron-mode coupling. The renormalized frequency reads [3, 4]:

$$\Omega_{\text{ren}} = \Omega_{\text{bare}} \sqrt{1 - \left(\frac{\varepsilon_{\text{gap}}}{4\varepsilon_{\text{JT}}}\right)^2},$$

as determined from the bottom curvature of the lateral vibronic wells.

\* Note a correction to the large-polaron condition of Ref. [3] due to D. Eagles.

## 7. Doping Dependence

The chief structural change in the vicinity of a planar hole is converting the associated  $\text{CuO}_6$  octahedron from tetragonal to cubic symmetry by removing the  $3d_{z^2} - 3d_{x^2-y^2}$  JT splitting. The restored  $3d$  degeneracy stimulates a hole flow to the  $3d_{z^2}$  orbital and to its coupled in-plane  $a_1$  ligand. This opens a way to axial hole leaks via the dynamic  $3d_{z^2} - 2p_z$  CT.

Due to the increasingly suppressed JT-distortion, i. e. the axial elongation of the  $\text{CuO}_6$  octahedron, the doping  $x$  shrinks the average  $\text{Cu(P)}-\text{O(A)}$  bond. With  $x$  standing for the number of free holes per  $\text{Cu(P)}$  atom, i. e. the probability for finding a hole in a given  $\text{CuO}_6$  octahedron, the average  $\text{Cu(P)}-\text{O(A)}$  axial bond length is

$$R_A(x) = (1-x)R_T + xR_C = R_T - (R_T - R_C)x$$

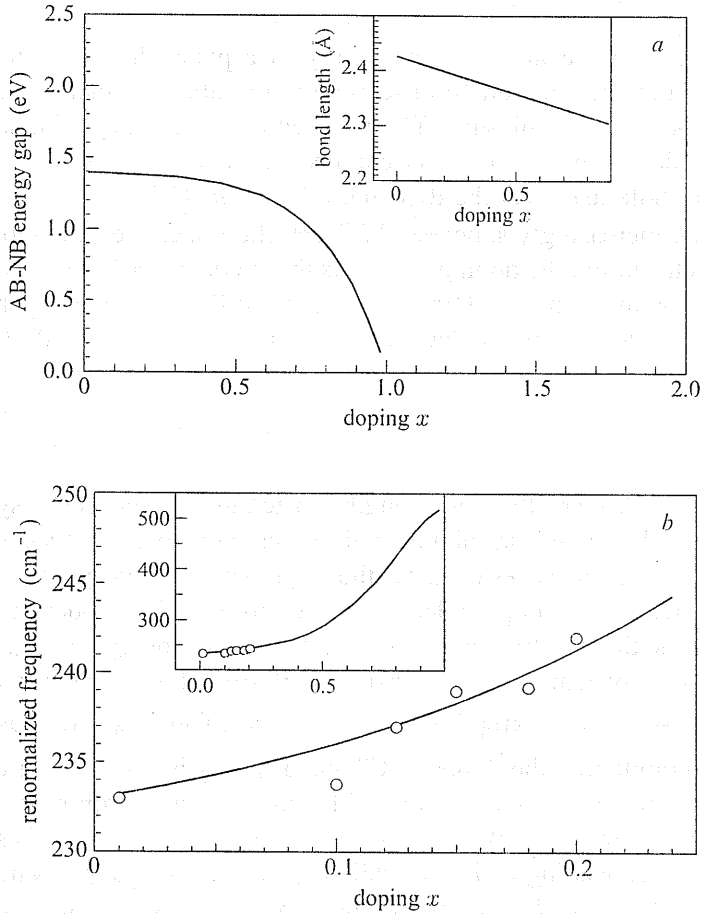
where  $R_T$  and  $R_C$  are the bond lengths in tetragonal and cubic symmetries, respectively. The bond shrinking tends to harmonize the lattice parameters along all the three axes resulting in the hypothetical cubic phase. The  $R(x)$  dependence results in a doping dependence of all bond-length-dependent quantities, such as the electron hopping  $t_{pd}$ , the ionic energy gap  $\varepsilon_{dp}$ , and the hybridized energy gap  $\varepsilon_{\text{gap}}$ . We take  $t_{pd}(x)$  from Fig. 1 and set tentatively  $\varepsilon_{pd}(x) = |\varepsilon_p - \varepsilon_d| \left[ 1 - \exp\left(-\frac{R^3(x) - R_C^3}{R_0^3}\right) \right]$  to calculate  $\varepsilon_{\text{AB-NB}}(x)$ , as shown in Fig. 2. Concomitantly, the dynamic CT band  $t_{\text{CT}}(x)$  is also doping dependent. The doping-suppressed JT distortion will also result in a drop of the electron-phonon mixing strength. We set  $G_{\text{JT}} \equiv G_{\text{JT}}(x) = (1-x)G_T$ , based on arguments as those leading to  $R(x)$ , while  $G_{\text{pJT}}(x)$  remains doping-independent.  $\Omega_{\text{ren}}/\Omega_{\text{bare}} \equiv \Omega_{\text{ren}}(x)/\Omega_{\text{bare}}(x)$  is doping-dependent, as shown above and in Fig. 2.

## 8. Dynamic Transfer Rate

Our approach to the dynamic transfer rate is based on an occurrence-probability (reaction rate) formula [10]. Introducing a renormalized frequency in the harmonic approximation, the transfer rate is

$$k_{12}(T) = \frac{1}{\pi} \Omega_{\text{ren}} \sinh \frac{\hbar \Omega_{\text{ren}}}{2k_B T} \sum_n W_{en}(E_n) W_{Ln}(E_n) \exp \frac{-E_n}{k_B T}$$

where  $E_n$  are the quantized energy levels,  $W_e$  is the probability for changing the electronic state from initial to final at the crossover coordinate  $Q_C$ ,  $W_L$  is the configurational tunneling probability.



**Fig. 2.** (a) Doping dependence of the energy gap  $\varepsilon_{\text{AB-NB}}(x)$ . Inset: Progenitor  $x$ -dependence of the Cu(P)-O(A) bond length  $R_A(x)$  originating from a free-hole suppressed Jahn-Teller distortion of the  $\text{CuO}_6$  octahedra. (b) Resulting doping dependence of the renormalized vibrational frequency  $\Omega_{\text{ren}}(x)$ . Inset:  $\Omega_{\text{ren}}(x)$  in an extended doping range

The circles are experimental data on the  $235 \text{ cm}^{-1}$  infrared axial mode in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  at 300 K (Ref. [5]). The fitting formulas are  $\varepsilon_{\text{NB-AB}} = \frac{1}{2} (\varepsilon_{pd} + \sqrt{\varepsilon_{pd}^2 + 8t_{pd}^2})$ ,  $\varepsilon_{pd} = (\varepsilon_d - \varepsilon_p) \left[ 1 - \exp\left(-\frac{R_A^3(x) - R_C^3}{R_0^3}\right) \right]$ , and  $R_A(x) = R_T(1-x) + R_Cx$  at model parameters:  $R_T = 2.426 \text{ \AA}$ ,  $R_C = 2.290 \text{ \AA}$ ,  $R_0 = 1.067 \text{ \AA}$ ,  $|\varepsilon_p - \varepsilon_d| = 1.482 \text{ eV}$ ,  $\varepsilon_{\text{JT}} = 0.390 \text{ eV}$ .  $\Omega_{\text{bare}} = 520 \text{ cm}^{-1}$  is the scale factor

To derive expressions feasible for numerical calculations, we first introduce



the Landau-Zener parameter

$$\gamma(E_n) = \frac{\varepsilon_{\text{AB-NB}}^2}{8\hbar\Omega_{\text{ren}}} \frac{1}{\sqrt{\varepsilon_R |E_n - \varepsilon_C|}}$$

in which  $\varepsilon_C$  is the crossover energy. For overbarrier transitions at  $E_n \gg \varepsilon_B$

$$W_e(E_n) = 2 \frac{1 - \exp(-2\pi\gamma)}{2 - \exp(-2\pi\gamma)},$$

while  $W_{L_n} \approx 1$ . For underbarrier transitions at  $E_n \ll \varepsilon_B$

$$W_e(E_n) = 2\pi\gamma^{2\gamma-1} \frac{\exp(-2\gamma)}{\Gamma^2(\gamma)},$$

while for parabolic wells with bottoms lying at the same energy

$$W_L(E_n) = \pi \left( \frac{F_{nm}(q_0, q_c)}{2^n n!} \right)^2 \exp\left(-\frac{\varepsilon_R}{\hbar\Omega_{\text{ren}}}\right).$$

Here  $n$  is the vibronic quantum number in the initial (final) electronic state,  $q_0 = q_2 - q_1$  is the interwell separation along  $Q$ .  $F_{nm}(q_0, q_c)$  is a quadratic form by Hermite polynomials.  $q = \sqrt{\frac{M\Omega_{\text{ren}}}{\hbar}} Q$  is a scaled mode coordinate.  $\varepsilon_R$  is the lattice reorganization energy.

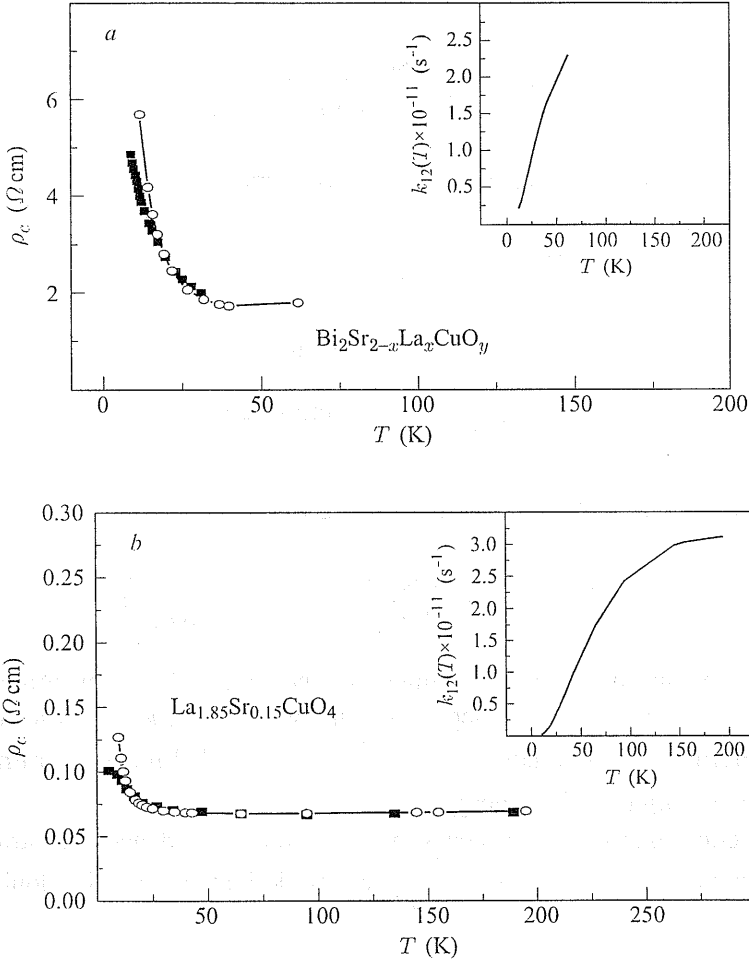
For practical purposes, we next summarize the dependences of various energy parameters on  $\varepsilon_{\text{JT}}$  and  $\mu = \frac{\varepsilon_{\text{gap}}}{4\varepsilon_{\text{JT}}}$ , easily derivable from the double-well geometry:

$$\begin{aligned} \varepsilon_B &= \varepsilon_{\text{JT}}(1 - \mu)^2, & \text{the interwell barrier} \\ \varepsilon_{\text{NB-AB}} &= 4\varepsilon_{\text{JT}}\mu, & \text{the interlevel gap energy} \\ \varepsilon_R &= 4\varepsilon_{\text{JT}}(1 - \mu^2), & \text{the lattice reorganization energy} \\ \varepsilon_C &= \varepsilon_{\text{JT}}(1 + \mu^2), & \text{the crossover energy} \end{aligned}$$

along with  $\hbar\Omega_{\text{ren}} = \hbar\Omega_{\text{bare}}\sqrt{1 - \mu^2}$ , the well-bottom (renormalized) vibrational frequency.

It is noteworthy that a finite zero-point rate of magnitude

$$k_{12}(0) = \frac{\Omega_{\text{ren}}}{2\pi} W_e(E_0) W_L(E_0)$$



**Fig. 3.** Temperature dependence of the axial resistivity  $\rho_c$

Experimental data at  $60T$  for  $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$  (a) and  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (b) from Ref. [7] are depicted by filled squares while our respective best fits by the double-well theory are represented by solid lines with open circles. The fitting parameters are:  $\varepsilon_B = 8.8$  meV,  $\mu = 0.3$ ,  $h\nu_{\text{ren}} = 1.5$  meV ( $\text{Bi}_2\text{Sr}_{1.85}\text{La}_{0.15}\text{CuO}_y$ ) and  $\varepsilon_B = 7.8$  meV,  $\mu = 0.4$ ,  $h\nu_{\text{ren}} = 2.5$  meV ( $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ ). The fitting formula is:  $\rho_c(T) = \rho_c(0) + A[T/k_{12}(T)]$  ( $A \propto k_B/eNR_{Ap}$ ) with  $A = 5.9 \times 10^9$   $\Omega\text{cm/K s}$  ( $\text{Bi}_2\text{Sr}_{1.85}\text{La}_{0.15}\text{CuO}_y$ ),  $A = 7.64 \times 10^6$   $\Omega\text{cm/K s}$  ( $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ ) and zero-point resistivities:  $\rho_c(0) = 0$  ( $\text{Bi}_2\text{Sr}_{1.85}\text{La}_{0.15}\text{CuO}_y$ ),  $\rho_c(0) = 0.065$   $\Omega\text{cm/K s}$  ( $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ ). Each inset presents the temperature dependence of the respective phonon-coupled electron-transfer rate  $k_{12}(T)$

at  $E_0 = \frac{1}{2} \hbar \Omega_{\text{ren}}$  is predicted, closely related to the small-polaron tunneling splitting  $t_{\text{CT}}$ . From the relevant equations for  $W_{e_0}$  and  $W_{L_0}$  we readily find

$$t_{\text{CT}} = \hbar \sqrt{\Omega_{\text{ren}} k_{12}(0)}$$

which is a novel result relating the reaction-rate formula to polaron physics.

The temperature dependence of the transfer rate  $k_{12}(T)$  is illustrated in Fig. 3 (insets) at parameters close to ones extracted from experimental resistivity data [7]. The metallic-like range discernible for  $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$  is rather scarce for  $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_y$ , due to the lack of reported experimental data.

## 9. Axial Resistivity

Given the net  $\text{Cu(P)} \rightarrow \text{O(A)}$  transfer rate  $\Delta k_{12}(x, T, \mathbf{F})$ , that is, the difference in the number of holes transferred per unit time forth and back in an electric field  $\mathbf{F}$  along the  $c$ -axis, the axial dc conductivity is

$$\sigma_c = eN(x)R_A \frac{\Delta k_{12}(x, T, \mathbf{F})}{F},$$

while the resistivity  $\rho_c$  is inversely proportional to  $\Delta k_{12}(x, T, \mathbf{F})xR_A(x)$ . Here  $N(x) \propto x$  is the carrier concentration,  $R_A$  is the  $\text{Cu(P)}\text{-O(A)}$  bond length. The thermal activation energy, viz. interwell barrier  $\varepsilon_B = \varepsilon_{\text{JT}}(1 - \mu)^2$ , varies with the doping  $x$  through  $\mu \equiv \mu(x) = \frac{\varepsilon_{\text{gap}}(x)}{4\varepsilon_{\text{JT}}(x)}$ , consistent with experimental observations [2].

Accounting for the field-dependent transfer rates, forth  $k_{12}^+(x, T, \mathbf{F}) = k_{12}(x, T) \exp(\mathbf{p} \cdot \mathbf{F} / 2k_B T)$  and back  $k_{12}^-(x, T, \mathbf{F}) = k_{12}(x, T) \exp(-\mathbf{p} \cdot \mathbf{F} / 2k_B T)$ , the difference in an external electric field  $\mathbf{F}$  along the  $c$ -axis reads:

$$\Delta k_{12}(x, T, \mathbf{F}) \equiv k_{12}^+(x, T, \mathbf{F}) - k_{12}^-(x, T, \mathbf{F}) = 2k_{12}(x, T) \sinh(\mathbf{p} \cdot \mathbf{F} / 2k_B T).$$

Here  $k_{12}(x, T)$  is the dynamic interwell transfer rate at  $\mathbf{F} = \mathbf{0}$  as introduced in Section 9, now dependent not only on the temperature but also on the doping.  $\mathbf{p}$  is the dipole associated with the anharmonic oscillator. At  $\mathbf{p} \cdot \mathbf{F} / 2k_B T \ll 1$ ,  $\Delta k_{12}(x, T, \mathbf{F}) \approx k_{12}(x, T)(\mathbf{p} / k_B T)F$ .

The temperature dependence of the axial resistivity is shown in Fig. 3 calculated at parameters deduced from the experimental data [7]. A semiconductor-like decreasing-resistivity lower-temperature range is seen followed by a metal-like range where  $\rho_c \propto T$ , as observed.

## 10. Implications

We present theoretical formulae for the doping dependences of the hybridized energy gap  $\varepsilon_{\text{AB-NB}}(x)$ , the dynamic CT band  $t_{\text{CT}}(x)$ , and the renormalized vibrational frequency  $\Omega_{\text{ren}}(x)$ , as well as for the temperature dependences of the dynamic CT rate  $k_{12}(T)$  and the axial resistivity  $\rho_c(T)$ .

The temperature dependence of the renormalized vibrational frequency  $\Omega_{\text{ren}}(T)$  is also dealt with as the average frequency of an ensemble of anharmonic oscillators with double-well potentials and a dipole-dipole coupling [11]. Calculations for a temperature dependence on this basis show  $\Omega_{\text{ren}}(T)$  to be virtually temperature-independent within a wide range followed by a steep decrease as  $T$  is raised beyond very high values (typically beyond 1000 K). Attempts to match the observed  $\Omega_{\text{exp}}(T)$  dependence by the ensemble model at any sensible magnitudes of the dipole-dipole coupling have failed. Consequently, we conclude that the observed drop of  $\Omega_{\text{exp}}(T)$  between 100–300 K has been associated with thermal dilation of the lattice rather than to renormalization effects in the statistical ensemble.

The  $c$ -axis resistivity problem has been addressed earlier by Zoli using the path integral method [12]. His model is similarly based on the coupling of fermionic excitations to double-well potentials associated with apical oxygens. He includes disorder by considering a distribution of double wells. Zoli's conclusions are similar to ours in that there is a negative temperature slope for the resistivity at low temperature at large coupling strengths, due to polaron trapping by the double wells. Experimental resistivity data have been collected in normal state [6], or within an extended temperature range by suppressing the superconductivity in an external magnetic field [7]. They clearly show a semiconducting behavior at the lower temperatures.

The CT gap is identified in NIR spectra and found to drop on doping, possibly as  $\varepsilon_{\text{gap}}(x)$ . More complex is the problem posed by the vibrational frequencies  $\Omega_{\text{ren}}(x, T)$  which may not be easily identified in optical conductivity spectra, if renormalization has degraded them down to the acoustic range. Yet, investigations over the accessible doping and temperature ranges have been performed on  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  [5]. Two odd axial modes at 500 and 235  $\text{cm}^{-1}$  have been deduced from IR spectra and found, respectively, to soften and harden with  $x$  or to harden and soften with  $T$ . These dependences are rather weak and are not obviously related to the superconducting transition. Our predictions are for a softening frequency as temperature is raised at fixed doping and hardening frequency as doping is increased at fixed temperature.

We believe our results will be found useful for analyzing the feasibility of the double-well concept to events along the  $c$ -axis. Further studies into the problem are now in progress and will be reported elsewhere.

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