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Two- and three-dimensional polaronic motion: Beyond the Holstein model

Marco Zoli*
Dipartimento di Matematica e Fisica, Sezione INFM, Universitá di Camerino, Via Madonna delle Carceri, 62032 Camerino, Italy

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The effects of dimensionality on small-polaron motion have been studied in the framework of the Holstein model in which the intermolecular forces act through a first-neighbors pair potential. A perturbative approach allows one to calculate the matrix elements determining both the polaronic band and the site-jump hopping probability as a function of temperature. It is found that the crossover temperature T_d^* between bandlike and diffusive motion is sensibly reduced in low-dimensional systems due to the enhanced importance of the off-diagonal scattering processes. By increasing the polaron binding energy the bandwidth narrows and the hopping probability quickly drops, hence T_d^* is shifted upwards. It is shown that the dispersion in the phonon spectrum is essential for the validity of the model. [S0163-1829(98)05713-0]

I. INTRODUCTION

During the last few years, the physics of (bi)polarons has been widely investigated in connection with the discovery of high-T_c superconductivity in ceramic compounds.[1–4] The local dynamics of the apical oxygen atom and the chain-copper cluster in some high-T_c materials would suggest the presence of polaron tunneling and nonadiabatic behavior in the electron-lattice system.[5,6] Structural and optical properties[7] together with anomalous c-axis electrical transport[8] have been interpreted in terms of nonlinear dynamic models relying on the concept of self-localization. A charge carrier is said to be self-trapped when it bounds within a potential well due to atomic displacements from their equilibrium positions. Since these displacements are caused by the presence of electrons the two features, potential well and electron wave function, must be determined self-consistently. The size of the region of lattice deformation induced by the carrier determines the polaron radius. If this size is *larger* than the lattice constant the polaron is referred to as large or of the Fröhlich type. In this case, the polaron problem can be treated by assuming the validity of the effective-mass and continuum approximations[9] and, in general, one is faced with the quantum-mechanical problem of a Fermi particle (the charge carrier) interacting with a boson field (the quantized crystal lattice). On the other hand, when the size of the lattice distortion is of the same order of (or less than) the lattice constant the polaron has a *small radius* and the discreteness of the lattice must be taken into account.[10] The electron-phonon interaction and the dimensionality of the system[11,12] determine the transition between the large radius state and the small radius state. In the ground state of the system the path-integral approach provides a powerful tool to investigate the properties of the polaron.[13,14] At finite temperatures, the transition between low-T bandlike motion and high-T diffusive motion can be described in the framework of the Holstein model or molecular crystal model (MCM).[15] The MCM, originally formulated for a one-dimensional system, is based on a discrete nonlinear Schrödinger equation which constitutes the foundation for several studies of physical and biological systems in which nonlinear effects take place[16–19] and self-trapped carriers determine the type of motion.[20] At sufficiently high temperatures the lattice vibrations can be treated classically, the motion is thermally activated and the hopping rate grows exponentially. In terms of the MCM, the transition temperature T^* is usually estimated as about 40% of the typical Debye temperature. However T^* could be influenced by the dimensionality of the system. The present study extends the MCM formalism to the two- and three-dimensional cases pointing out the consequences on the transition between bandlike and hopping motion.

II. THE MODEL AND THE RESULTS

In the molecular crystal model, the system is a lattice of N identical diatomic molecules whose internuclear displacement coordinates deviate from their equilibrium values. The state of the system is described by

$$\psi(\mathbf{r},\mathbf{x}_1\cdots\mathbf{x}_N)=\sum_j a_j(\mathbf{x}_1\cdots\mathbf{x}_N)\,\phi(\mathbf{r}-j\mathbf{b},\mathbf{x}_j), \tag{1}$$

where $\mathbf{r}$ is the electron coordinate, $\mathbf{x}_j$ is the internuclear deviation from equilibrium at the jth molecular site, $\mathbf{b}$ is a unit lattice vector, ϕ is the electron wave function localized at the jth site and the coefficients a_j of the superposition obey the time-dependent Schrödinger equation:

$$\left(i\hbar\,\frac{\partial}{\partial t}-\sum_{l=1}^{N}\left[-\frac{\hbar^2}{2M}\nabla_l^2+\frac{M\omega_0^2}{2}\,\mathbf{x}_l^2\right]-E(\mathbf{x}_j)\right)\cdot a_j(\mathbf{x}_1\cdots\mathbf{x}_N)$$
$$=\sum_{l\neq j} J(\mathbf{x}_l,\mathbf{x}_j)\,a_l(\mathbf{x}_1\cdots\mathbf{x}_N). \tag{2}$$

M is the reduced molecular mass and ω_0 is the Einstein phonon frequency. $E(\mathbf{x}_j)$ is the electron energy at the jth lattice site and it is assumed as a linear function of the internuclear vibrational coordinate, $E(\mathbf{x}_j)=-A|\mathbf{x}_j|$. A is a positive constant measuring the strength of the electron-lattice interaction and determining the binding energy of the polaron which is given, in essence, by $E_b=A^2/(2M\omega_0^2)$. $J(\mathbf{x}_l,\mathbf{x}_j)$ is the electronic overlap integral of the tight-binding approximation and it describes the electronic motion through the lattice. The J's dependence on the lattice vibration coor-

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dinates can been neglected.[15] $2nJ$ is the bare electron bandwidth with n being the coordination number. Then, the polaron state properties are essentially specified by the parameters A, J, and ω_0. In particular, if $nJ>E_b$ the polaron dimension is larger than the lattice spacing and the polaron is of the Fröhlich type, whereas the small-polaron regime is attained once the condition $nJ<E_b$ is fulfilled. Input parameters satisfying the latter condition will be chosen in the following. In the case of a large electron effective mass and strong electron-phonon coupling, relevant to narrow-band materials, J can be treated as the perturbation. It should be remarked that a perturbative approach requires even more restrictive conditions on the smallness of J.[21] Therefore only the lower part of the range of J values, for which the polaron is small, can be consistently used in a perturbative solution of Eq. (2). I consider a model in which first-neighbor molecular sites interact through a pair potential. This introduces a dispersion in the optical-phonon frequencies whose expressions are given, in the one-, two-, and three-dimensional system, respectively, by

$$\omega^2_{1\mathrm{D}}(k)=\frac{\alpha+\gamma}{M}+\frac{1}{M}\sqrt{\alpha^2+2\alpha\gamma\cos kb+\gamma^2},$$

$$\omega^2_{2\mathrm{D}}(\mathbf{k})=\frac{\alpha+2\gamma}{M}+\frac{1}{M}\sqrt{\alpha^2+2\alpha\gamma(\cos k_xb+\cos k_yb)+2\gamma^2[1+\cos(k_xb-k_yb)]},$$

$$\omega^2_{3\mathrm{D}}(\mathbf{k})=\frac{\alpha+3\gamma}{M}+\frac{1}{M}\sqrt{\alpha^2+2\alpha\gamma(\cos k_xb+\cos k_yb+\cos k_zb)+\gamma^2[3+l(\mathbf{k})]},$$

$$l(\mathbf{k})=2\cos(k_xb-k_yb)+2\cos(k_xb-k_zb)+2\cos(k_yb-k_zb). \qquad (3)$$

The intramolecular force constant α and the intermolecular first-neighbor force constant γ are input parameters of the theory. In terms of the Einstein phonon frequency, α is given by the relation, $\omega_0^2=2\alpha/M$. An isotropic interaction model has been implicitly assumed both in the square lattice and in the simple cubic lattice.

The three-dimensional (3D) matrix elements, which are responsible for the site jump (from j to j') induced by the perturbation J, are given in momentum space representation by

$$\begin{aligned}\langle j..N_k..|V|j'..N'_k..\rangle=-J\sum_m\prod_k\Bigg[&\delta_{N_{k_x},N'_{k_x}}\delta_{N_{k_y},N'_{k_y}}\delta_{N_{k_z},N'_{k_z}}\left(1-\frac{f^2(m,\mathbf{k})}{4}(2N'_{k_x}+1)\right)\left(1-\frac{f^2(m,\mathbf{k})}{4}(2N'_{k_y}+1)\right)\\&\times\left(1-\frac{f^2(m,\mathbf{k})}{4}(2N'_{k_z}+1)\right)+\delta_{N_{k_x},N'_{k_x}}\delta_{N_{k_z},N'_{k_z}}\left(\sqrt{\frac{N'_{k_y}}{2}}\delta_{N_{k_y},N'_{k_y}-1}-\sqrt{\frac{N'_{k_y}+1}{2}}\delta_{N_{k_y},N'_{k_y}+1}\right)\\&\times\left(1-\frac{f^2(m,\mathbf{k})}{4}(2N'_{k_x}+1)\right)\left(1-\frac{f^2(m,\mathbf{k})}{4}(2N'_{k_z}+1)\right)f(m,\mathbf{k})+\delta_{N_{k_x},N'_{k_x}}\delta_{N_{k_y},N'_{k_y}}\\&\times\left(\sqrt{\frac{N'_{k_z}}{2}}\delta_{N_{k_z},N'_{k_z}-1}-\sqrt{\frac{N'_{k_z}+1}{2}}\delta_{N_{k_z},N'_{k_z}+1}\right)\left(1-\frac{f^2(m,\mathbf{k})}{4}(2N'_{k_x}+1)\right)\\&\times\left(1-\frac{f^2(m,\mathbf{k})}{4}(2N'_{k_y}+1)\right)f(m,\mathbf{k})+\delta_{N_{k_y},N'_{k_y}}\delta_{N_{k_z},N'_{k_z}}\left(\sqrt{\frac{N'_{k_x}}{2}}\delta_{N_{k_x},N'_{k_x}-1}-\sqrt{\frac{N'_{k_x}+1}{2}}\delta_{N_{k_x},N'_{k_x}+1}\right)\\&\times\left(1-\frac{f^2(m,\mathbf{k})}{4}(2N'_{k_y}+1)\right)\left(1-\frac{f^2(m,\mathbf{k})}{4}(2N'_{k_z}+1)\right)f(m,\mathbf{k})\Bigg],\end{aligned} \qquad (4)$$

$$f(m,\mathbf{k})=\left(\frac{4M\omega_k}{N\hbar}\right)^{1/2}\frac{A}{M\omega_k^2}\sin(\mathbf{k}\cdot m\mathbf{b}/2)[\sin(\mathbf{k}\cdot m\mathbf{b}/2)+\cos(\mathbf{k}\cdot mb/2)].$$

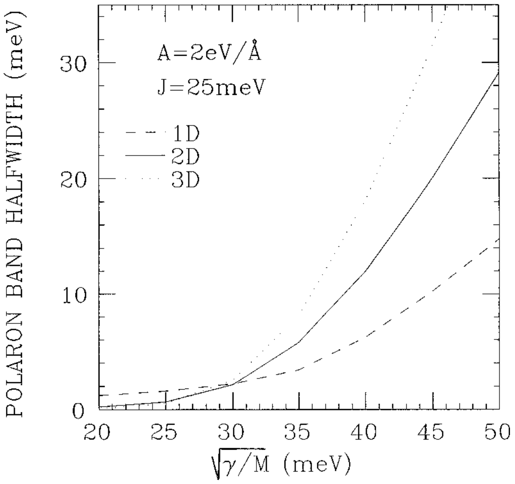

FIG. 1. Ground-state polaron band halfwidths, in one, two, and three dimensions, versus the first-neighbor intermolecular interaction energy. γ is the force constant. The intramolecular interaction energy is $\hbar\omega_0 = 50$ meV.

The m summation runs over first neighbors molecular sites and $N_{\mathbf{k}}$ is the number of $\mathbf{k}$ quanta. The 2D matrix elements are obtained from Eq. (4) by suppressing the oscillator polarized along the z axis. Then the intersite tunneling is due either to scattering processes in which the phonon occupation numbers do not change (diagonal transitions) or to processes in which some of these numbers change by one (off diagonal transitions). In the two- and three-dimensional systems, only processes in which at most one oscillator changes its quantum numbers have been retained: these yield the lowest-order contributions proportional to $1/N$.

At $T=0$, the phonon occupation numbers are all zero and only diagonal transitions can take place. Hence, from Eq. (4), the ground-state polaron band halfwidth is given by

$$\Delta E_{n,d} = nJ\,\exp\left[-\frac{1}{N}\sum_{k_x}\sin^2(k_x b/2)\sum_{k_y,k_z}\frac{dA^2\hbar^2}{M(\hbar\omega(\mathbf{k}))^3}\right], \tag{5}$$

where d is the dimensionality of the system. Summation over k_z pertains to the 3D case only. The electron-lattice coupling induces exponential renormalization of the intersite tunneling and narrowing of the polaronic band. Accordingly, the polaron moves slowly through the lattice and localization at the site is likely to occur. This effect is expected to be more pronounced in low-dimensional systems where the number of overlapping polaronic wave functions is reduced. However, we point out that the contraction of the band is strongly influenced by the phonon spectrum. In Fig. 1, the ground-state polaron bands in 1D, 2D, and 3D are plotted versus γ, the parameter which determines the dispersion in the phonon frequencies. We choose the values $A = 2$ eV Å^{-1}, $\hbar\omega_0 = 50$ meV, and $J = \hbar\omega_0/2$ which guarantee a small-polaron regime. It is seen that the bands grow by increasing γ but, below a certain value of $\simeq 30$ meV, the 1D ground-state band turns out to be larger than the 2D and 3D bands. In other words the polaron band broadens, as expected, as a function of d only if intermolecular interactions are sufficiently strong. This suggests that quantitative polaronic models should be very sensitive to the detailed structure of the vibrational spectrum and the phonon dispersion is essential in providing realistic models of polaronic motion. A pure Einstein model or even a model with weak intermolecular couplings seem therefore inappropriate in this context. The intermolecular vibration energy $\sqrt{\gamma/M} = 30$ meV is therefore the *threshold value* for the validity of the model. Obviously this value depends on ω_0. In the following calculations, a value $\sqrt{\gamma/M} = 35$ meV will be assumed. Note that the polaron band halfwidth is substantially smaller than the bare electronic value nJ. The antiadiabatic inequality $\Delta E_{n,d} < \hbar\omega_0$ is fulfilled for the polaron.

At finite T, the polaron band halfwidth due to diagonal scattering processes is

$$\Delta E^T_{n,d} = nJ\,\exp\left[-\frac{1}{N}\sum_{k_x}\sin^2(k_x b/2)\times\sum_{k_y,k_z}\frac{dA^2\hbar^2}{M(\hbar\omega(\mathbf{k}))^3}\coth\frac{\beta\hbar\omega(\mathbf{k})}{2}\right], \tag{6}$$

where β is the inverse temperature. By increasing T the bandwidth diminishes whereas the off-diagonal transitions in Eq. (4) (whose probability is proportional to the Bose thermal factors) become more relevant. The diagonal processes contribute to the real part of the polaron self-energy whereas the off-diagonal hops, contributing to the imaginary part of the self-energy, determine the polaron lifetime τ_p. When a temperature T^* is attained in which $\tau_p \simeq \hbar/\Delta E^T$ the polaron band description breaks down and the polaron moves via a succession of random site jumps. The site jump probability, due to nondiagonal transitions between localized states, can be calculated perturbatively. The result is

$$W(j\to j') = \frac{nJ^2}{\hbar^2}\exp\left[-\frac{1}{N}\sum_{k_x}(1-\cos k_x b)\times\sum_{k_y,k_z}\frac{dA^2\hbar^2}{M(\hbar\omega(\mathbf{k}))^3}\coth\frac{\beta\hbar\omega(\mathbf{k})}{2}\right].$$

$$\int_{-\infty}^{+\infty}d\tau\left\{\exp\left[\frac{1}{N}\sum_{k_x}(1-\cos k_x b)\sum_{k_y,k_z}\times\frac{dA^2\hbar^2}{M(\hbar\omega(\mathbf{k}))^3}\,\mathrm{csch}\,\frac{\beta\hbar\omega(\mathbf{k})}{2}\cos(\omega(\mathbf{k})\tau)\right]-1\right\}, \tag{7}$$

where τ is the time during which perturbation theory applies. Actually the integration range does not extend to infinity, the numerical convergence of the time integral being fast enough. The cutoff $\tau^{\max}$ depends on dimensionality and weakly on temperature. Equations (6) and (7) have been computed as a function of temperature for several sets of input parameters. In Fig. 2, I have assumed the same parameters as in Fig. 1 which yield a polaron binding energy of $\simeq 209$ meV for an oxygen molecular solid. The intermolecular vibration energy has been fixed at 35 meV. It can be seen that T^* grows with dimensionality being $T^*_{1D} \simeq 100$ K, $T^*_{2D} \simeq 130$ K, and $T^*_{3D} \simeq 150$ K. The typical Debye temperature is 580 K. The polaron band narrows by lowering d although the

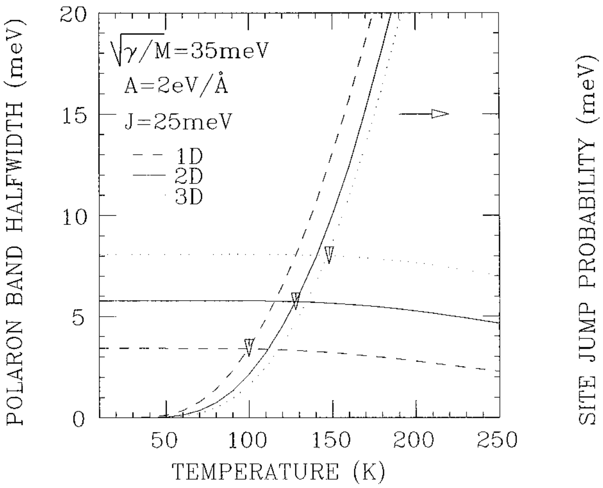

FIG. 2. Polaron band halfwidths and site jump probabilities (times $\hbar$) versus temperature in 1D, 2D, and 3D. The triangles mark the crossover temperatures between bandlike and hopping regimes.

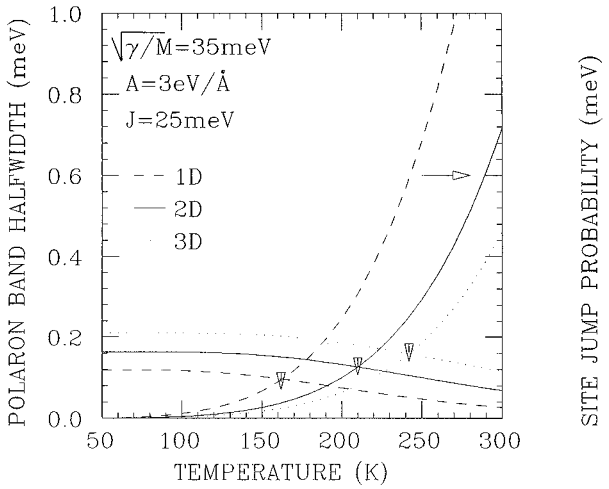

FIG. 3. As in Fig. 2 but with $A=3$ eV Å^{-1}.

percentual halfwidth $\Delta E^T_{n,d}/nJ$ is 5.4×10^{-2} in 3D, 5.8×10^{-2} in 2D and 6.8×10^{-2} in 1D (at $T=10$ K). The cutoff in the interaction time shortens as a function of d being, at $T=10$ K, $\tau^{\max}_{1D}=2\times10^{-14}$ s, $\tau^{\max}_{2D}=1.6\times10^{-14}$ s and $\tau^{\max}_{3D}=1.38\times10^{-14}$ s. This means that numerical convergence of the time integral in Eq. (7) is achieved by using 203 points in 1D, 162 points in 2D, and 138 points in 3D. Nonetheless, computation of the hopping probability in 3D is much more time consuming because of the momentum space summations. The shortening of $\tau^{\max}_d$ by increasing d follows from the fact that the phonon spectrum dispersion essentially damps the oscillating behavior of the argument in the exponential as a function of τ and such dispersion gets larger by increasing d. In fact, from Eqs. (3), one gets

$$\omega^2_d(k_x=k_y=k_z=0)-\omega^2_d(k_x=k_y=k_z=\pi)=2d\gamma/M, \tag{8}$$

and this suggests that stronger intermolecular forces also reduce the maximum interaction time. For instance, taking $\sqrt{\gamma/M}=45$ meV, we get $\tau^{\max}_{2D}=1.3\times10^{-14}$ s at $T=10$ K. A dispersionless phonon spectrum would not permit a convergence in the $d\tau$ integration thus confirming the inadequacy of an Einstein model for the boson field. By enhancing γ, T^*_d is shifted towards higher temperatures. Moreover, as Fig. 3 shows, a substantial variation of T^*_d occurs if the electron-lattice coupling is increased. Setting A at 3 eV Å^{-1} yields a polaron binding energy of $\simeq 470$ meV and, as a consequence, we get $T^*_{1D}\simeq170$ K, $T^*_{2D}\simeq210$ K, and $T^*_{3D}\simeq245$ K. In this case the percentual halfwidths of the bands, at $T=10$ K, are $\Delta E^T_{6,3}/6J=1.4\times10^{-3}$, $\Delta E^T_{4,2}/4J=1.6\times10^{-3}$ and $\Delta E^T_{2,1}/2J=2.2\times10^{-3}$. Note that the energy scale in Fig. 3 is smaller by a factor 20 than in Fig. 2 hence, stronger electron-lattice coupling causes both narrowing of the band and decreasing of the site jump probability. Then, the lifetime of the localized polaron state gets longer and off-diagonal scattering, which destroys the coherence of the wave function, becomes effective only at higher temperatures. Finally, I have studied the behavior of T^*_d as a function of the transfer integral J. The results are summarized in Fig. 4: T^*_d decays by increasing J and tends to stabilize at J values which fulfill the adiabatic condition $nJ\gg\hbar\omega_0$ for the bare electrons. In that range however the present perturbative approach does not apply.[21] We observe that narrow-band electronic systems exhibit the highest T^*_d and that the difference $T^*_{3D}-T^*_{2D}$ is smaller than $T^*_{2D}-T^*_{1D}$. Both differences slightly decrease versus J, being $T^*_{3D}-T^*_{2D}=23$ K and $T^*_{2D}-T^*_{1D}=36$ K at $J=10$ meV, $T^*_{3D}-T^*_{2D}=15$ K and $T^*_{2D}-T^*_{1D}=22$ K at $J=60$ meV.

III. CONCLUSIONS

I have studied the polaron motion in 1D, 2D, and 3D by taking into account the discreteness of the lattice and the role of the intermolecular coupling strengths. The dispersion of the optical-phonon frequencies is fundamental in order to estimate correctly the ground-state polaron band in d dimensions. This result is consistent with a recent study by Alexandrov pointing out the inadequacy of the dispersionless Holstein model in evaluating the small- (bi)polaron mass.[22] The bare electronic transfer integral of the tight-binding approximation, the electron-lattice coupling, and the intramolecular vibrational energy, which are the input parameters of

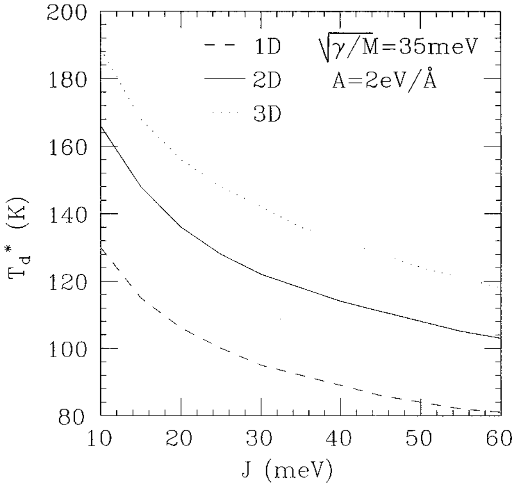

FIG. 4. Crossover temperatures between bandlike and hopping motion versus the overlap electronic integral J, in 1D, 2D, and 3D.

our model, have been chosen to satisfy the condition for the existence of the small polaron. The perturbative method, the transfer integral being the perturbation, has been applied to evaluate the matrix elements responsible for the polaron band narrowing and the hopping probability from site to site. We observe that both the polaronic energy band and the hopping conductivity are rather sensitive to the value of the overall electron-lattice coupling which determines the binding energy of the polaron. The transition T_d^* between the low-temperature range, in which a bandlike description holds, and the high-temperature range, in which the motion is thermally activated, strongly depends (i) on the dimensionality of the system, (ii) on the binding energy of the small polaron, and (iii) on the bare electronic bandwidth. T_d^* decreases by reducing d, being 150 K in 3D, 130 K in 2D, and 100 K in 1D if a polaron binding energy of $\simeq 0.2$ eV is assumed. By doubling the binding energy, T_d^* is shifted upwards of about 70–80 K and narrowing the electronic band results in a further increase of T_d^*. In view of the exponential growth of the site jump probability versus temperature, the width of the transition region is negligible so that either a bandlike or a hopping motion is expected as the signature for polaron transport.

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*Electronic address: ZOLI@CAMSERV.UNICAM.IT

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