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ORIGINAL PAPER

Transition Between Large and Small Polaron States in the Electronic Structure of HTSC Cuprates

I. A. Makarov[1] · E. I. Shneyder[1] · P. A. Kozlov[1] · S. G. Ovchinnikov[1]

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Abstract The effect of strong electron correlations (SEC) and strong electron-phonon interaction (EPI) on the electronic structure of cuprates is studied within the polaronic version of the generalized tight binding method. Both diagonal and off-diagonal EPI in terms of ionic coordinates are considered.

Keywords Cuprates · Strong electron correlations · Electron-phonon interaction · Polaron · Franck-Condon process · Hubbard fermions · Band structure

1 Introduction

There is no consensus regarding the role of the electron-phonon interaction in the formation of the electronic structure and superconducting properties of the HTSC cuprates. The main reason of contradictions is the lack of reliable information about magnitude of electron-phonon interaction (EPI) constant. Indirect evidences of EPI influence on electronic system has been provided by ARPES experiments. Broad peak and Gaussian line shape of the ARPES spectra has been explained in the framework of the phenomenological approach [3] that uses scenario of Franck-Condon broadening. These and other features were also reproduced in the theoretical works using t-J-model with on-site electron-phonon coupling [4, 5]. Polaronic features of the spectra of undoped HTSC cuprates indicate strong interaction between carriers and phonons in these systems. In this work, we investigate local electronic structure and band structure of undoped cuprates in the framework of polaronic generalized tight-binding method (p-GTB) with taking into account diagonal and off-diagonal EPI. Such approach expands possibilities of the Holstein model and provides more realistic description of cuprates and other strongly correlated oxides.

2 Hamiltonian of the Three-Band Model with EPI

GTB method [6] includes three stages: exact diagonalization of a separate cluster, construction of the Hubbard operators that describe the Fermi- and Bose-excitations within the cluster, and cluster perturbation theory. In the polaronic version of GTB, the Hamiltonian of strongly correlated holes interacting with optical phonons is considered, basis states of cluster are given by a product of hole and phonon wave functions. We consider CuO_2 plane which models single layer HTSC compound, namely La_2CuO_4. Each elementary cell consists of one copper and four oxygen atoms; each oxygen atom simultaneously belongs to two elementary cells. Electron system is considered in the framework of the three-band p-d-model [7, 8], which describe low-energy excitations in the CuO_2 plane. This model includes Cu-$d_{x^2-y^2}$ and O-p_x, p_y orbitals. Phonon subsystem includes local dispersionless optical phonons of the oxygen breathing mode. There are two types of EPI in our system: diagonal and off-diagonal. Diagonal EPI results from renormalization of copper on-site energy by the oxygen displacements from their equilibrium positions. Off-diagonal EPI results from hopping integral modulation with changing of Cu-O bond length. To orthogonalize oxygen wave functions in the

✉ I. A. Makarov
macplay@mail.ru

[1] Kirensky Institute of Physics, 660036 Krasnoyarsk, Russia

neighbor clusters, we introduce molecular oxygen orbitals for the electron orbitals [1]

$$a_{\mathbf{q}\sigma} = -\frac{i}{\mu_{\mathbf{q}}}\left(s_y p_{(x)\mathbf{q}\sigma} + s_x p_{(y)\mathbf{q}\sigma}\right),$$
$$b_{\mathbf{q}\sigma} = \frac{i}{\mu_{\mathbf{q}}}\left(s_x p_{(x)\mathbf{q}\sigma} - s_y p_{(y)\mathbf{q}\sigma}\right), \quad (1)$$

and for the phonon states [2]

$$A_{\mathbf{q}} = -\frac{i}{\mu_{\mathbf{q}}}\left(s_x e_{(x)\mathbf{q}} + s_y e_{(y)\mathbf{q}}\right),$$
$$B_{\mathbf{q}} = -\frac{i}{\mu_{\mathbf{q}}}\left(s_y e_{(x)\mathbf{q}} - s_x e_{(y)\mathbf{q}}\right). \quad (2)$$

where $e_{x(y)}$ is operator of phonon creation for the $p_{x(y)}$-orbitals. After orthogonalization total Hamiltonian can be written as a sum of the interactions inside CuO_4 cluster H_c and the intercluster contribution H_{cc}

$$H = H_c + H_{cc}, H_c = \sum_{\mathbf{f},\sigma} H_{\mathbf{f}\sigma}, H_{cc} = \sum_{\mathbf{f},\mathbf{g},\mathbf{h},\sigma} H_{\mathbf{fgh}\sigma},$$
$$\begin{aligned} H_{\mathbf{f}\sigma} &= \varepsilon_d d^\dagger_{\mathbf{f}\sigma} d_{x\mathbf{f}\sigma} + \varepsilon_b b^\dagger_{\mathbf{f}\sigma} b_{\mathbf{f}\sigma} \\ &\quad -T_b\left(d^\dagger_{\mathbf{f}\sigma} b_{\mathbf{f}\sigma} + h.c.\right) \\ &\quad +U_d d^\dagger_{\mathbf{f}\uparrow} d_{\mathbf{f}\uparrow} d^\dagger_{\mathbf{f}\downarrow} d_{\mathbf{f}\downarrow} + U_b b^\dagger_{\mathbf{f}\uparrow} b_{\mathbf{f}\uparrow} b^\dagger_{\mathbf{f}\downarrow} b_{\mathbf{f}\downarrow} \\ &\quad +\sum_{\sigma'} \tilde{V}_{pd} d^\dagger_{\mathbf{f}\sigma} d_{\mathbf{f}\sigma} b^\dagger_{\mathbf{f}\sigma'} b_{\mathbf{f}\sigma'} \\ &\quad +\hbar\omega_{br} A^\dagger_{\mathbf{f}} A_{\mathbf{f}} + 2g_d\mu_{00}\left(A^\dagger_{\mathbf{f}} + A_{\mathbf{f}}\right) n^\sigma_{(d)\mathbf{f}} \\ &\quad +2g_{pd}\rho^A_0\left(A^\dagger_{\mathbf{f}} + A_{\mathbf{f}}\right)\left(d^\dagger_{\mathbf{f}\sigma} b_{\mathbf{f}\sigma} + h.c.\right), \\ H_{\mathbf{fgh}\sigma} &= -2t_{pd}\mu_{\mathbf{fg}}\left(d^\dagger_{\mathbf{f}\sigma} b_{\mathbf{g}\sigma} + h.c.\right) \\ &\quad -2t_{pp}\nu_{\mathbf{fg}}\left(b^\dagger_{\mathbf{f}\sigma} b_{\mathbf{g}\sigma} + h.c.\right) \\ &\quad +2g_d\mu_{\mathbf{fg}}\left(A^\dagger_{\mathbf{f}} + A_{\mathbf{f}}\right) n^\sigma_{(d)\mathbf{g}} \\ &\quad +2g_{pd}\rho^A_{\mathbf{fgh}}\left(A^\dagger_{\mathbf{f}} + A_{\mathbf{f}}\right)\left(d^\dagger_{\mathbf{g}\sigma} b_{\mathbf{h}\sigma} + h.c.\right). \end{aligned} \quad (3)$$

Since contribution of the a_{1g}-orbital to spectral weight of quasiparticle excitations at low temperature is negligible, we exclude this orbital along with B-type phonons from the basis and from the Hamiltonian (3). The energy parameters in (3) are defined as $\varepsilon_b = \varepsilon_p - 2t_{pp}\nu_{00}$, $\tau_b = 2t_{pd}\mu_{00}$, $U_b = U_p\Psi_{0000}$, $\tilde{V}_{pd} = V_{pd}\Phi_{000}$. Coefficients μ_{00}, ν_{00}, ρ^A_0, Ψ_{0000}, Φ_{000} are values of structural factors $\mu_{\mathbf{fg}}$, $\nu_{\mathbf{fg}}$, $\rho^A_{\mathbf{fgh}}$, $\Psi_{\mathbf{ijkl}}$, $\Phi_{\mathbf{ijk}}$ for single cluster, $\mu_{00} = 0.958$, $\nu_{00} = 0.727$, $\rho^A_0 = -0.457$, $\Psi_{0000} = 0.2109$, $\Phi_{000} = 0.918$. Values of $\Psi_{\mathbf{ijkl}}$, $\Phi_{\mathbf{ijk}}$ are strongly decreased with distance increasing. The model parameters are $\varepsilon_d = 0$, $\varepsilon_p = 1.5$ eV, $t_{pd} = 1.36$ eV, $t_{pp} = 0.86$ eV, $U_d = 9$ eV, $U_p = 4$ eV, and $V_{pd} = 1.5$ eV [9]. Energy of breathing mode phonon $\hbar\omega_{br} = 90$ meV. [10] It is convenient to define the dimensionless parameter of electron-phonon interaction which will be used throughout this work as a measure of the electron-phonon coupling strength,

$$\lambda_{d(pd)} = \frac{g^2_{d(pd)}}{2M\omega^2_{br}W}, \quad (4)$$

where M–mass of oxygen atom. For the chosen set of parameters, the bandwidth W of the occupied valence band in La_2CuO_4 has been calculated by the LDA+GTB method and is equal to 2.2 eV.

Hole basis wave function $|\beta\rangle$ are defined in sectors of Hilbert space with hole number $n_h = 0, 1, 2$:

$$|\beta\rangle = \begin{cases} |0\rangle, n_h = 0 \\ |d\rangle, |b\rangle, n_h = 1 \\ |ZR\rangle, |d_\downarrow d_\uparrow\rangle, |b_\downarrow b_\uparrow\rangle, n_h = 2 \end{cases}, \quad (5)$$

where $|ZR\rangle = \frac{1}{\sqrt{2}}\left(|d_\downarrow b_\uparrow\rangle - |d_\uparrow b_\downarrow\rangle\right)$ is the Zhang-Rice singlet. Phonon basis wave functions are

$$|\nu\rangle = \frac{1}{\sqrt{\nu!}}\left(A^\dagger\right)^\nu |0\rangle, \quad (6)$$

where $A^\dagger$ is the operator of A-type phonon creation.

3 Local Polaron States

In the frameworks of such description, exact local multi-electron eigenstate i of the CuO_4 cluster is polaron state:

$$|n_h, i\rangle = \sum_{\beta\nu} c^\beta_{i\nu}|\beta\rangle|\nu\rangle \quad (7)$$

The ground and excited eigenstates (7) characterize the hole surrounded by a cloud of phonons, e.g., the polaron

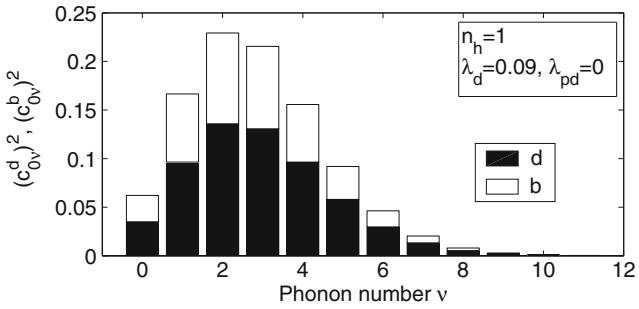

Fig. 1 The distribution of a hole among copper d and oxygen b orbitals namely probabilities $(c^d_{0\nu})^2$, $(c^b_{0\nu})^2$ as function of the phonon number ν in the ground single-hole state $|1\sigma, 0\rangle$ at $\lambda_d = 0.09$ and $\lambda_{pd} = 0$

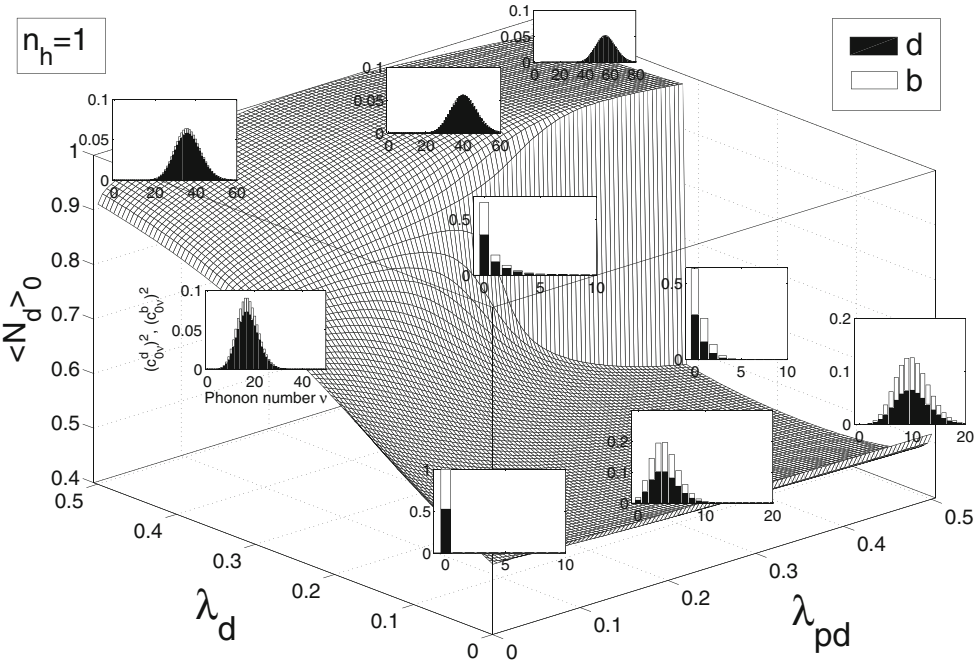

Fig. 2 Surface of the average number of holes on the d-orbital $\langle N_d \rangle_0$ for the single-hole ground state in the space of parameters $\lambda_d - \lambda_{pd}$ with structures of the ground state for some characteristic points of this space

(Fig. 1). Structure of polaron state strongly depends on magnitude of EPI constant λ_d and λ_{pd} and their ratio. It is convenient to describe polaron states by the average number of holes on copper $\langle N_d \rangle$ which is analogue of localization degree as a result of self-trapping for our system. Surface of the average number of holes in the space of parameters $\lambda_d - \lambda_{pd}$ shows influence of EPI on distribution of hole density in the cluster. As seen from Fig. 2, surface of average hole number on copper d-orbital $\langle N_d \rangle_0$ for the single-hole ground state consists of two regions. First region of $\langle N_d \rangle_0$ is defined at smaller λ_d. Cluster eigenstates in this weak localization region are large local polaron states with insignificant increasing of copper occupation at EPI increasing and with small phonon cloud. Second region is strong localization region defined at larger λ_d and it is formed by small local polaron states. Small polaron state is characterized by the cluster eigenstates with massive phonon cloud and almost fully occupied copper orbital. Transition between states from the different regions can be smooth or abrupt depending on λ_{pd}.

At $\lambda_{pd} < (\lambda_{pd})_c$, we have smooth transition from large local polaron to small polaron. λ_d increasing leads to transformation of eigenstate itself: small phonon cloud spreads, hole density is gradually transferred to multiphonon components and occupation of copper orbital increases. At $\lambda_{pd} > (\lambda_{pd})_c$, character of transition between large and small polaron states in the ground single-hole eigenstate is different, i.e. abrupt. Calculations show that massive phonon cloud with all hole density on d-orbital is formed in the structure of high-energy excited states with large average number of phonons $\langle N_{ph} \rangle$i. With λ_d increasing energy of small local polaron state decreases. This level crosses series of the excited cluster eigenstates that actually leads to multiple crossovers. Two trends corresponding small and large local polaron states can be seen in

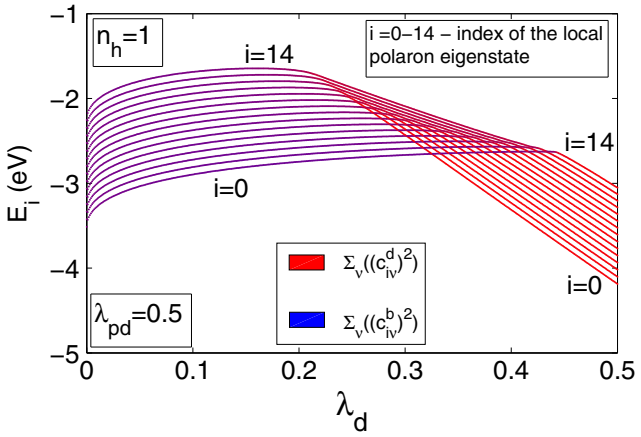

Fig. 3 The dependence of energy levels of a single hole (i=0) and 14 excited states on diagonal EPI λ_d at $\lambda_{pd} = 0.5$. The crossover between large and small local polaron states occurs near $(\lambda_d)_c = 0.314$. *Red component of composite color of each point of* $E_i(\lambda_d)$ *curve* is defined by the sum (over phonon index ν) of the probability amplitudes at multiphonon basis states with d-orbital of copper. *Blue component of color* is defined by the sum of the probability amplitudes at basis states with b-orbital of oxygen. *Red lines* show energy of small local polaron states with almost full occupation of d-orbital. *Purple lines* show energies of the large polaron state and states with complex distribution of the hole density

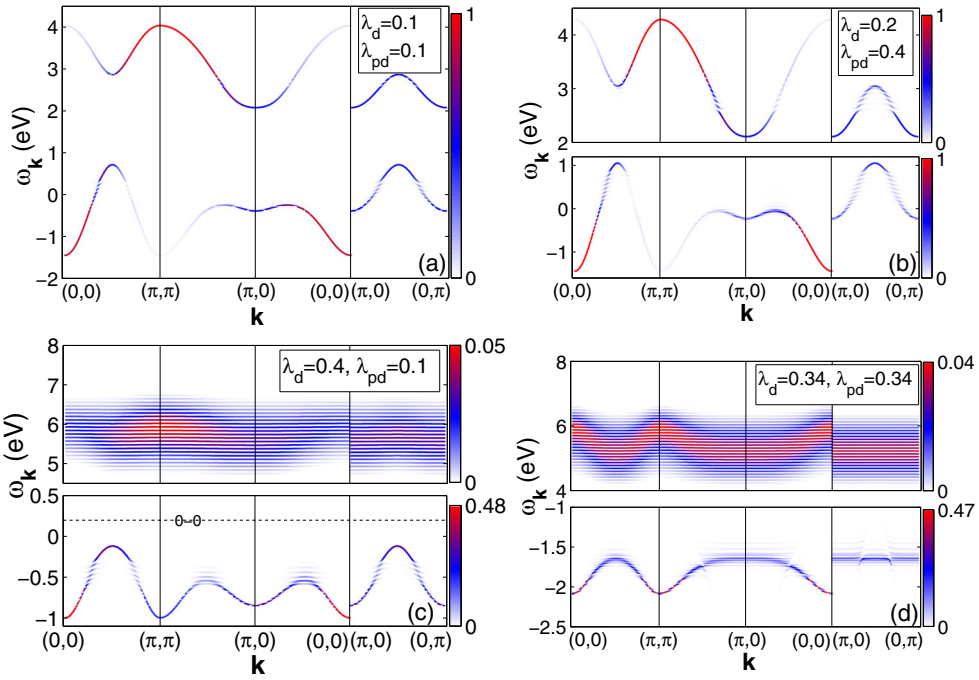

Fig. 4 Effect of diagonal and off-diagonal EPI on the polaron band structure of the undoped antiferromagnetic La_2CuO_4 at $T = 10$ K for different EPI constants values: **a** $\lambda_d = 0.1$, $\lambda_{pd} = 0.1$, **b** $\lambda_d = 0.2$, $\lambda_{pd} = 0.4$, **c** $\lambda_d = 0.4$, $\lambda_{pd} = 0.1$, and **d** $\lambda_d = 0.34$, $\lambda_{pd} = 0.34$. *Dashed horizontal line* in (**c**) shows dispersionless band of quasiparticles corresponding to $0 - 0$ Franck-Condon resonance; this excitations has negligible intensity and large effective mass

the dependencies of energies of ground and excited single-hole eigenstates on EPI (Fig. 3). Small local polaron state becomes the ground state at $\lambda_d > (\lambda_d)_c \sim 0.31$. Large local polaron state is the ground state at $\lambda_d < (\lambda_d)_c$ and its energy depends very weakly on diagonal EPI. Note that $(\lambda_d)_c$ almost does not depend on λ_{pd} in the single-hole sector of Hilbert space.

For the two-hole bipolaron ground state, the border between weak and strong localization regions depends on λ_d as well as on λ_{pd}. At small λ_{pd}, critical value $(\lambda_d)_c$ is more than in the single-hole case because strong Coulomb repulsion prevents bipolaron formation. With λ_{pd} increasing, the hole density is transferred to oxygen orbitals, contribution from Coulomb repulsion U_d becomes weaker and consequently $(\lambda_d)_c$ decreases. At the critical point $\lambda_d = (\lambda_d)_c$, there is a crossover between the eigenstates with different two-hole configurations. At $\lambda_d < (\lambda_d)_c$, the main probability of hole occupation in the ground state is on Zhang-Rice singlet, whereas at $\lambda_d > (\lambda_d)_c$ the $|d_\downarrow d_\uparrow\rangle$-configuration acquires the maximal occupation. The copper holes number increases sharply almost by 1 at the critical point. Thus, effective attraction mediated by EPI wins competition with the Coulomb repulsion for two-hole eigenstates.

Possible structures of polaron states and scenario of transition between large and small local polaron states are qualitatively stable with respect to variation of parameters of electron model $\Delta = \varepsilon_p - \varepsilon_d$ and t_{pd}. Decreasing of t_{pd} leads to shift of $(\lambda_d)_c$ and $(\lambda_{pd})_c$ to smaller values. Growth of charge-transfer energy increase occupation of copper orbital and consequently $(\lambda_d)_c$ decreases, whereas $(\lambda_{pd})_c$ increases.

4 Polaronic Band Structure

Relative polaronic effect for the eigenstates of Hilbert space sectors with different fermion number is of great importance for the formation of band structure. Multiphonon Fermi-type quasiparticle excitations between local polaron states of the cluster with $n_h = 0, 1, 2$ are processes of the Franck-Condon type. Dispersion of polaron quasiparticles in the antiferromagnetic phase has been obtained with the equation of motion method for the two-sublattice matrix retarded Green function of polarons in the Hubbard I approximation. Band structure of polaron quasiparticles is the result of hybridization between Hubbard fermions and local multiphonon Franck-Condon resonances. The main polaronic effect of the quasiparticle band structure is splitting of the Hubbard bands on the number of Hubbard polaron subbands.

Since features of electronic structure are largely determined by the structure of local polaron states, we investigate band structure of polaron quasiparticles in the four characteristic points of $\lambda_d - \lambda_{pd}$ parameters space: (a) $\lambda_d = 0.1$, $\lambda_{pd} = 0.1$, (b) $\lambda_d = 0.2$, $\lambda_{pd} = 0.4$, (c) $\lambda_d = 0.4$, $\lambda_{pd} = 0.1$, and (d) $\lambda_d = 0.34$, $\lambda_{pd} = 0.34$. In the point (a), single-hole and two-hole ground states are large polarons with small phonon clouds, insignificantly different from the case without EPI [9]. Effects of diagonal and off-diagonal

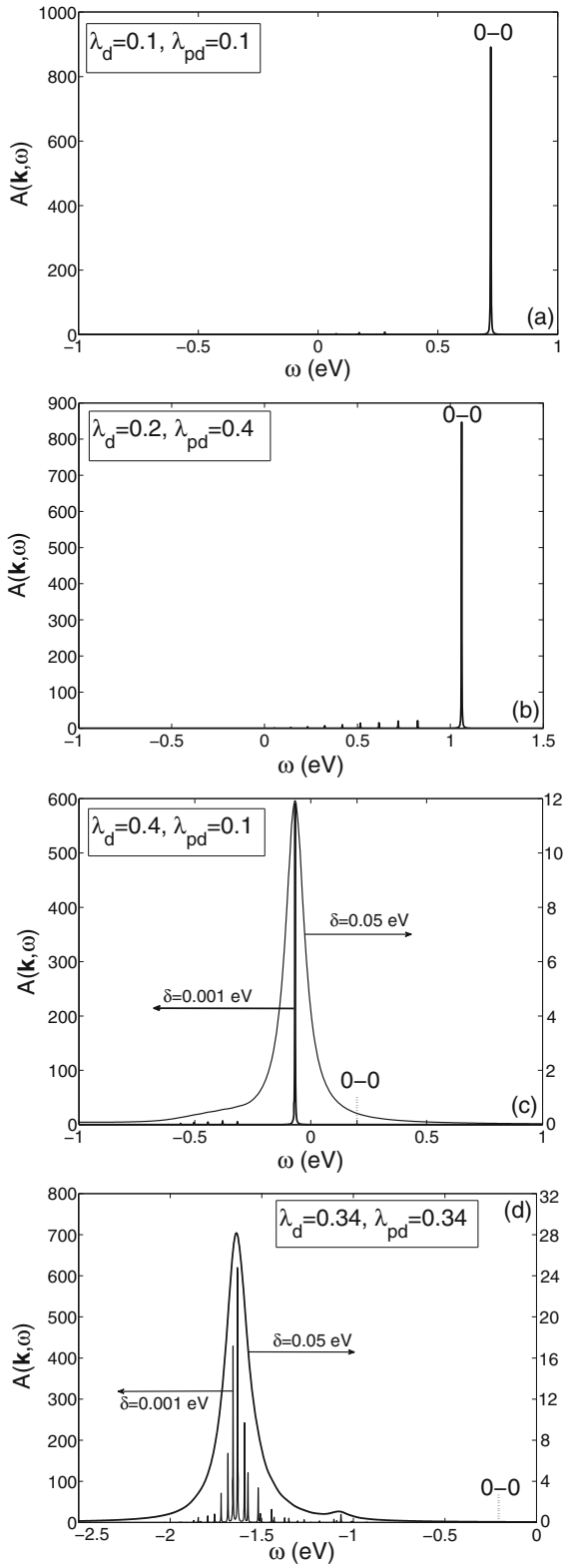

Fig. 5 The spectral function of the first removal state at $\left(\frac{\pi}{2}, \frac{\pi}{2}\right)$ for **a** $\lambda_d = 0.1, \lambda_{pd} = 0.1$, **b** $\lambda_d = 0.2, \lambda_{pd} = 0.4$, **c** $\lambda_d = 0.4, \lambda_{pd} = 0.1$, **d** $\lambda_d = 0.34, \lambda_{pd} = 0.34$. The multiphonon Franck-Condon resonances have negligible intensity for delocalized polaron at (**a**) and appears for localized polaron at (**b**). At (**c**), and (**d**) 0-0 resonance has zero intensity; its position is marked by the *vertical bar*

EPI largely compensate each other. Therefore, band structure reconstruction is weakly expressed (Fig. 4a). Splitting of the Hubbard fermion bands to the hybridized subbands results in the series of narrow peaks for a given momentum **k** (Fig. 5a–c). Spectral function of polaron quasiparticles at $\mathbf{k} = \left(\frac{\pi}{2}, \frac{\pi}{2}\right)$ is high-intensity coherent peak related to $0 - 0$ Franck-Condon resonance (excitation between ground single-hole and two-hole states) at the top of the valence band and tiny peaks at the energies of multiphonon Franck-Condon resonances (Fig. 5a).

In the case (b) of large polaron with large phonon cloud, off-diagonal EPI increases probabitity on the multiphonon components of the local states while *b*-orbital occupation increasing. It results in appearing of intensity of the multiphonon processes in the valence band (Fig. 5b) and increasing of number and magnitudes of splittings (Fig. 4b).

Overlap of the wave functions of single-hole and two-hole local eigenstates disappears in the strong localization region (point (c)) due to different occupation of copper orbitals and consequently different polaronic effect in these states. The low-energy excitations in the top of the valence band and bottom of the conductivity band acquire large effective mass, lose spectral weight, and *k*-dependence (dashed line in Fig. 4c). Therefore, coherent peak of $0 - 0$ Franck-Condon process disappears (Fig. 5c). Main spectral weight is transferred to high-energy multiphonon excitations (Fig. 5c); however, it is seen that dispersion is maintained (Fig. 4c) despite of bandwidth decreasing. Intensity attenuation occurs due to distribution of spectral weight over more number of points in the *k*-space. In the point (d), polaron excitations in the wide range of energies have large effective mass, negligible intensity. Dispersion of Hubbard polaron bands is strongly modified; however, memory about band structure without EPI is still noticeable (Fig. 4d).

The effect of the quasiparticle finite lifetime modeled by the different Lorenzian width δ results in formation of one wide peak in the spectral function from the sum of several Franck-Condon resonances for large λ values (Fig. 5d). Similar broad peak is seen in ARPES experiments. Form and width of the broad peak of the spectral function strongly depends on wave vector **k** and EPI value.

5 Conclusion

Structure of the local polaron states and band structure of polaron excitations are investigated in the different regions of space of parameters $\lambda_d - \lambda_{pd}$. Two types of local polaron states have been identified in the space of parameters $\lambda_d - \lambda_{pd}$: states with weak localization ($\lambda_d < (\lambda_d)_c$) and states with strong localization ($\lambda_d > (\lambda_d)_c$). Transition

between these two types of polaron states with λ_d increasing can be smooth ($\lambda_{pd} < (\lambda_{pd})_c$) or abrupt (crossover at $\lambda_{pd} > (\lambda_{pd})_c$). Crossover between large and small local polaron states is obtained for the local eigenstates of CuO_4 cluster. Strong electron correlations (SEC), many-particle effects, and polaronic effects in the local states significantly influence on the band structure forming. Band structure has different type depending on magnitude and ratio of $\lambda_d - \lambda_{pd}$ parameters. The general effect of EPI constant increasing on the band structure is the growth of the number and magnitude of splittings, transfer of the spectral weight to the multiphonon excitations, and over number of k-points, reduction of the Hubbard band and polaron subbands widths. At ($\lambda_{pd} < (\lambda_{pd})_c$) λ_d, increasing leads to low-energy excitations at the top of the valence band and at the bottom of the conductivity band gradually acquire large effective mass, lose dispersion, and intensity. At ($\lambda_{pd} > (\lambda_{pd})_c$) λ_d, increasing brings to effective mass of the quasiparticles in the wide energy range abruptly increases; all spectral weight is on high-energy multiphonon excitations. Characteristic type of band structure and spectral function at certain k-points can serve as indicator of strength of EPI in systems with SEC and strong EPI.

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