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Multiphonon contribution to the polaron formation in cuprates with strong electron correlations and strong electron-phonon interaction

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ABSTRACT

In this work dependences of the electron band structure and spectral function in the HTSC cuprates on magnitude of electron-phonon interaction (EPI) and temperature are investigated. We use three-band p-d model with diagonal and off-diagonal EPI with breathing and buckling phonon mode in the frameworks of polaronic version of the generalized tight binding (GTB) method. The polaronic quasiparticle excitation in the system with EPI within this approach is formed by a hybridization of the local multiphonon Franck-Condon excitations with lower and upper Hubbard bands. Increasing EPI leads to transfer of spectral weight to high-energy multiphonon excitations and broadening of the spectral function. Temperature effects are taken into account by occupation numbers of local excited polaronic states and variations in the magnitude of spin-spin correlation functions. Increasing the temperature results in band structure reconstruction, spectral weight redistribution, broadening of the spectral function peak at the top of the valence band and the decreasing of the peak intensity. The effect of EPI with two phonon modes on the polaron spectral function is discussed.

Keywords: high-temperature superconductivity, cuprates, strong electronic correlations, cluster form of perturbation theory, Hubbard operator, three-band p-d model, electron-phonon interaction, polaron, Franck-Condon broadening

1. INTRODUCTION

One of the main features of the electronic spectra of undoped HTSC cuprates is a large width of spectral function peak at the top of valence band (lower Hubbard band, LHB) comparable with bandwidth value, its Gaussian shape [1] and its large temperature dependence [2,3]. Strong electron-phonon interaction (EPI) results in polaronic states formation. Since polaronic effect depends on fermion number and charge distribution the excitations between different multielectron states are also multiphonon. This concept of Franck-Condon broadening was suggested in [1] and theoretical description of broadening in the frameworks of t-J-Holstein model was made in [4,5].

Large temperature dependence of electronic spectra includes broadening of the peak, shift of its position and the decrease of its intensity. All these effects were qualitatively described in the [5,6] taking into account the Bose-Einstein thermal distribution of phonons. However qualitative effect of the linewidth doubling with temperature increasing from 200 to 400 K wasn't explained.

In this work we investigate the temperature dependence of the polaronic band structure and spectral function within the three-band p-d model with diagonal and off-diagonal EPI for breathing local oxygen mode using a polaronic version of generalized tight-binding method (p-GTB). Besides population of excited polaronic states we will also take into account influence of temperature on the spin-spin correlation functions. Also dependence of spectral function on magnitude of diagonal EPI with two modes, breathing and buckling, is considered.

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2. THREE-BAND P-D MODEL WITH DIAGONAL AND OFF-DIAGONAL EPI

Low-energy electronic structure of HTSC cuprates in the normal phase and their properties in the superconducting phase are defined by electronic states at the top of the valence band. These states are related to excitations (holes) that are distributed over hybridized orbitals including copper $d_{x^2-y^2}$ (hereinafter d) and oxygen $p_{x,y}$ orbitals inside the CuO_2 plane. As the vibrations of breathing and buckling oxygen modes are known the most strongly couple with charge carriers, we will consider the EPI of dispersionless local breathing and buckling modes which results from vibrations of the light O atoms relative to the fixed heavy Cu atoms. Displacement of O atoms changes value of the crystal field for the hole on Cu atom, the hopping integral between copper and oxygen atomic orbitals and Coulomb interaction between holes on copper and oxygen atoms. We take into account diagonal (renormalization of on-site energy on Cu atom with surrounding oxygen atoms) and off-diagonal renormalization of the p-d hopping integral) EPI and neglect renormalization of Coulomb interaction.

Thus we will use the three-band p-d-Holstein model plus diagonal and off-diagonal EPI with breathing mode phonons and diagonal EPI with buckling mode phonons:

$$
\begin{gathered}
H = H_e + H_{ph} + H_{e-ph} \\
H_{el} = \sum_{\mathbf{f}\sigma} \varepsilon_d d^\dagger_{\mathbf{f}\sigma} d_{\mathbf{f}\sigma} + \sum_{\alpha\mathbf{h}\sigma} \varepsilon_p p^\dagger_{\alpha\mathbf{h}\sigma} p_{\alpha\mathbf{h}\sigma} + \\
\sum_{\mathbf{fh}\alpha\sigma} (-1)^{R_\mathbf{h}} t_{pd} \left(d^\dagger_{\mathbf{f}\sigma} p_{\alpha\mathbf{h}\sigma} + H.c. \right) + \sum_{\alpha\alpha'\mathbf{h}\neq\mathbf{h}'\sigma} (-1)^{M_{\mathbf{hh}'}} t_{pp} \left(p^\dagger_{\alpha\mathbf{h}\sigma} p_{\alpha'\mathbf{h}'\sigma} + H.c. \right) + \\
\sum_{\mathbf{f}} U_d d^\dagger_{\mathbf{f}\uparrow} d_{\mathbf{f}\uparrow} d^\dagger_{\mathbf{f}\downarrow} d_{\mathbf{f}\downarrow} + \sum_{\mathbf{h}} U_p p^\dagger_{\alpha\mathbf{h}\uparrow} p_{\alpha\mathbf{h}\uparrow} p^\dagger_{\alpha\mathbf{h}\downarrow} p_{\alpha\mathbf{h}\downarrow} + \sum_{\alpha\mathbf{fh}\sigma\sigma'} V_{pd} d^\dagger_{\mathbf{f}\sigma} d_{\mathbf{f}\sigma} p^\dagger_{\alpha\mathbf{h}\sigma'} p_{\alpha\mathbf{h}\sigma'} \qquad (1) \\
H_{ph} = \frac{M}{2} \sum_{\mathbf{h}} \left(\dot{u}^2_{\mathbf{h}} + \omega_b^2 \dot{u}^2_{\mathbf{h}} \right) + \frac{M}{2} \sum_{\mathbf{h}} \left(\dot{z}^2_{\mathbf{h}} + \omega_a^2 \dot{z}^2_{\mathbf{h}} \right) \\
H_{e-ph} = \sum_{\mathbf{f}\sigma} \left(\sum_{\mathbf{h}} (-1)^{S_\mathbf{h}} g_d u_{\mathbf{h}} \right) d^\dagger_{\mathbf{f}\sigma} d_{\mathbf{f}\sigma} - \sum_{\mathbf{fh}\sigma} (-1)^{R_\mathbf{h}} (-1)^{S_\mathbf{h}} g_{pd} u_{\mathbf{h}} \left(d^\dagger_{\mathbf{f}\sigma} p_{\alpha\mathbf{h}\sigma} + H.c. \right) + \\
\sum_{\mathbf{f}\sigma} \left(\sum_{\mathbf{h}} g_a z_{\mathbf{h}} \right) d^\dagger_{\mathbf{f}\sigma} d_{\mathbf{f}\sigma}
\end{gathered}
$$

Here $d_{\mathbf{f}\sigma}$ and $p_{\alpha\mathbf{h}\sigma}$ are the operators of hole annihilation with spin σ on d-orbital of the copper atom $\mathbf{f}$ and p_x (p_y)-orbital of the oxygen atom $\mathbf{h}$, respectively. Vector $\mathbf{h}$ runs over two of the four positions of planar oxygen atoms neighboring to Cu atom in octahedral unit cell centered on site $\mathbf{f}$ at each α, $\mathbf{h} = \left\{ \left(f_x - a/2, f_y \right), \left(f_x + a/2, f_y \right) \right\}$ if $\alpha = x$, $\mathbf{h} = \left\{ \left(f_x, f_y - b/2 \right), \left(f_x, f_y + b/2 \right) \right\}$ if $\alpha = y$, a and b are the lattice parameters. ε_d is the on-site energy of hole on Cu ion and ε_p is the on-site energy of hole on O ion; t_{pd} is the amplitude of hopping between d-orbitals of Cu ion $\mathbf{f}$ and $p_{x,y}$-orbitals of O ion $\mathbf{h}$ in CuO_2 plane and t_{pp} is the amplitude of hopping between neighboring $p_{x,y}$-orbitals of the oxygen atoms $\mathbf{h}$ and $\mathbf{h}'$. The phase parameters $R_\mathbf{h}$ and $M_{\mathbf{hh}'}$ are determined by phases of overlapping wave functions; $R_\mathbf{h} = 0$ for $\mathbf{h} = \left(f_x - a/2, f_y \right), \left(f_x, f_y + b/2 \right)$ and $R_\mathbf{h} = 1$ for $\mathbf{h} = \left(f_x + a/2, f_y \right), \left(f_x, f_y - b/2 \right)$, $M_{\mathbf{hh}'} = 0$ for hoppings $\left(f_x - a/2, f_y \right) - \left(f_x, f_y - b/2 \right)$, $\left(f_x + a/2, f_y \right) - \left(f_x, f_y + b/2 \right)$ and $M_{\mathbf{hh}'} = 1$ for hoppings $\left(f_x - a/2, f_y \right) - \left(f_x, f_y + b/2 \right)$, $\left(f_x + a/2, f_y \right) - \left(f_x, f_y - b/2 \right)$. U_d is the Coulomb interaction of two holes on the same copper atom and U_p is the same for oxygen atom, V_{pd} is the intersite Coulomb interaction when one hole is on the copper orbital and other hole is on the oxygen orbital. $u_\mathbf{h} = \sqrt{\frac{\hbar}{2M\omega_b}} \left(e^\dagger_{\alpha\mathbf{h}} + e_{\alpha\mathbf{h}} \right)$ is the operator of oxygen atom $\mathbf{h}$

displacement for breathing mode, $z_{\mathbf{h}} = \sqrt{\frac{\hbar}{2M\omega_a}}\left(f^{\dagger}_{\alpha\mathbf{h}} + f_{\alpha\mathbf{h}}\right)$ is the same for buckling mode, M is the mass of oxygen atom. $e^{\dagger}_{\alpha\mathbf{h}}$ ($f^{\dagger}_{\alpha\mathbf{h}}$) is the operator of creation of local phonon with frequency ω_b (ω_a) of breathing (buckling) mode. α denotes direction of atom $\mathbf{h}$ displacement. g_d (g_{pd}) is the parameter of the diagonal (off-diagonal) EPI with breathing mode. g_a is the parameter of the diagonal EPI with buckling mode. The phase parameter $S_{\mathbf{h}} = 0$ for $\mathbf{h} = \left(f_x + a/2, f_y\right), \left(f_x, f_y + b/2\right)$ and $S_{\mathbf{h}} = 1$ for $\mathbf{h} = \left(f_x - a/2, f_y\right), \left(f_x, f_y - b/2\right)$ is consistent with modulation of the on-site energy and hopping integrals for the breathing mode. We introduce dimensionless EPI parameters $\lambda_{d(pd)} = \left(g_{d(pd)}\xi\right)^2 \Big/ W\hbar\omega_b$ and $\lambda_a = \left(g_a\xi_a\right)^2 \Big/ W\hbar\omega_a$, where $\xi_b = \sqrt{\frac{\hbar}{2M\omega_b}}$ and $\xi_a = \sqrt{\frac{\hbar}{2M\omega_a}}$, W is the bandwidth of the free electron in tight-binding method without EPI, we choose here $W = 1$ eV, the breathing mode phonon energy $\hbar\omega_b = 0.04$ eV, the buckling mode phonon energy $\hbar\omega_a = 0.07$ eV. We use parameters of Hamiltonian (1) obtained from LDA+GTB method [7] for La_2CuO_4 (in eV):

$$\begin{gathered} \varepsilon_d = 0,\ \varepsilon_p = 1.5,\ t_{pd} = 1.36,\ t_{pp} = 0.86 \\ U_d = 9,\ U_p = 4,\ V_{pd} = 1.5 \end{gathered} \tag{2}$$

3. SCHEME OF THE POLARONIC VERSION OF GTB METHOD FOR HTSC CUPRATES

The GTB method was developed in [7-9] to calculate electronic structure of the systems with strong electron correlations. This method includes several stages. The first step is to divide the total Hamiltonian of the crystal into Hamiltonian of separate clusters and Hamiltonian of intercluster hopping and interactions. In the CuO_2 plane of La_2CuO_4 each oxygen atom belongs to two CuO_6 cluster. Therefore to represent crystal lattice of atoms in the form of complex of separate cluster it is necessary to perform the orthogonalization procedure. We introduce molecular oxygen orbitals $\left|b_{\mathbf{f}}\right\rangle$ and $\left|a_{\mathbf{f}}\right\rangle$ by transformation of the hole atomic oxygen orbitals $\left|p_{x\mathbf{h}}\right\rangle$ and $\left|p_{y\mathbf{h}}\right\rangle$ in the k-space [10]:

$$\begin{aligned} b_{\mathbf{k}} &= \frac{i}{\mu_{\mathbf{k}}}\left(s_{\mathbf{k}x}p_{x\mathbf{k}} - s_{\mathbf{k}y}p_{y\mathbf{k}}\right) \\ a_{\mathbf{k}} &= -\frac{i}{\mu_{\mathbf{k}}}\left(s_{\mathbf{k}y}p_{x\mathbf{k}} + s_{\mathbf{k}x}p_{y\mathbf{k}}\right) \end{aligned} \tag{3}$$

where $s_{\mathbf{k}x} = \sin\left(k_x a/2\right)$, $s_{\mathbf{k}y} = \sin\left(k_y b/2\right)$ and $\mu_{\mathbf{k}} = \sqrt{s^2_{\mathbf{k}x} + s^2_{\mathbf{k}y}}$. States $b_{\mathbf{f}}$ ($a_{\mathbf{f}}$) in the neighbor CuO_6 clusters are orthogonal to each other. Phonon states are orthogonalized by similar transformation where operators $A_{\mathbf{k}}$ and $B_{\mathbf{k}}$ in the momentum space are defined by transformation:

$$\begin{aligned} A_{\mathbf{k}} &= -\frac{i}{\mu_{\mathbf{k}}}\left(s_{\mathbf{k}x}e_{x\mathbf{k}} + s_{\mathbf{k}y}e_{y\mathbf{k}}\right) \\ B_{\mathbf{k}} &= -\frac{i}{\mu_{\mathbf{k}}}\left(s_{\mathbf{k}y}e_{x\mathbf{k}} - s_{\mathbf{k}x}e_{y\mathbf{k}}\right) \end{aligned} \tag{4}$$

$$\begin{aligned} C_{\mathbf{k}} &= \frac{1}{\upsilon_{\mathbf{k}}}\left(c_{\mathbf{k}x}f_{x\mathbf{k}} + c_{\mathbf{k}y}f_{y\mathbf{k}}\right) \\ D_{\mathbf{k}} &= \frac{1}{\mu_{\mathbf{k}}}\left(c_{\mathbf{k}y}f_{x\mathbf{k}} - c_{\mathbf{k}x}f_{y\mathbf{k}}\right) \end{aligned} \tag{5}$$

Here $c_{\mathbf{k}x} = \cos\left(k_x a/2\right)$, $c_{\mathbf{k}y} = \cos\left(k_y b/2\right)$ and $\upsilon_{\mathbf{k}} = \sqrt{c_{\mathbf{k}x}^2 + c_{\mathbf{k}y}^2}$. Local «atomic» phonons $e_{\alpha\mathbf{h}}^{\dagger}\left|0\right\rangle$ are replaced by «molecular» phonon wave functions $A_{\mathbf{f}}^{\dagger}\left|0\right\rangle$ and $B_{\mathbf{f}}^{\dagger}\left|0\right\rangle$ and phonons $f_{\alpha\mathbf{h}}^{\dagger}\left|0\right\rangle$ are replaced by «molecular» phonon wave functions $C_{\mathbf{f}}^{\dagger}\left|0\right\rangle$ and $D_{\mathbf{f}}^{\dagger}\left|0\right\rangle$. Contribution of phonons $B_{\mathbf{f}}^{\dagger}\left|0\right\rangle$ and $D_{\mathbf{f}}^{\dagger}\left|0\right\rangle$ to the low-energy local cluster eigenstates that are involved in formation of the electron spectral function at the top of the valence band and the bottom of the conduction band is negligible. Therefore we exclude $B_{\mathbf{f}}^{\dagger}\left|0\right\rangle$ and $D_{\mathbf{f}}^{\dagger}\left|0\right\rangle$ states from the consideration and retain only $A_{\mathbf{f}}^{\dagger}\left|0\right\rangle$ and $C_{\mathbf{f}}^{\dagger}\left|0\right\rangle$ phonon states.

The Hamiltonian of three-band model plus diagonal and off-diagonal EPI after orthogonalization procedure has form:

$$\begin{gathered} H = \sum_{\mathbf{f}\sigma} \varepsilon_d d_{\mathbf{f}\sigma}^{\dagger} d_{\mathbf{f}\sigma} + \sum_{\mathbf{f}\sigma} \varepsilon_p b_{f\sigma}^{\dagger} b_{f\sigma} - 2t_{pd} \sum_{\mathbf{fg}\sigma} \mu_{\mathbf{fg}} \left(d_{\mathbf{f}\sigma}^{\dagger} b_{\mathbf{g}\sigma} + H.c. \right) - 2t_{pp} \sum_{\mathbf{fg}\sigma} \nu_{fg} \left(b_{\mathbf{f}\sigma}^{\dagger} b_{\mathbf{g}\sigma} + H.c. \right) + \\ \sum_{\mathbf{f}} U_d d_{\mathbf{f}\uparrow}^{\dagger} d_{\mathbf{f}\uparrow} d_{\mathbf{f}\downarrow}^{\dagger} d_{\mathbf{f}\downarrow} + \sum_{\mathbf{fghl}} U_p \Psi_{\mathbf{fghl}} b_{\mathbf{f}\uparrow}^{\dagger} b_{\mathbf{g}\uparrow} b_{\mathbf{h}\downarrow}^{\dagger} b_{\mathbf{l}\downarrow} + \sum_{\mathbf{fgh}\sigma\sigma'} V_{pd} \Phi_{\mathbf{fgh}} d_{\mathbf{f}\sigma}^{\dagger} d_{\mathbf{f}\sigma} b_{\mathbf{g}\sigma'}^{\dagger} b_{\mathbf{h}\sigma'} + \\ \sum_{\mathbf{f}} \hbar\omega_b A_{\mathbf{f}}^{\dagger} A_{\mathbf{f}} + \sum_{\mathbf{fg}} 2g_d \xi_d \mu_{\mathbf{fg}} \sum_{\sigma} \left(A_{\mathbf{f}}^{\dagger} + A_{\mathbf{f}} \right) d_{\mathbf{g}\sigma}^{\dagger} d_{\mathbf{g}\sigma} + \sum_{\mathbf{fgh}} 2g_{pd} \xi_d \rho_{\mathbf{fgh}}^{A} \sum_{\sigma} \left(A_{\mathbf{f}}^{\dagger} + A_{\mathbf{f}} \right) \left(d_{\mathbf{g}\sigma}^{\dagger} b_{\mathbf{h}\sigma} + H.c. \right) \end{gathered} \tag{6}$$

where structural factors μ_{fg}, ν_{fg}, ρ_{fgh} are defined as

$$\mu_{\mathbf{fg}} = \frac{1}{N} \sum_{\mathbf{k}} \mu_{\mathbf{k}} e^{-i\mathbf{k}(\mathbf{f}-\mathbf{g})}$$

$$\nu_{\mathbf{fg}} = \frac{1}{N} \sum_{\mathbf{k}} \left(\frac{1}{\mu_{\mathbf{k}}} \sin\left(\frac{k_x}{2}\right) \sin\left(\frac{k_y}{2}\right) \right)^2 e^{-i\mathbf{k}(\mathbf{f}-\mathbf{g})}$$

$$\rho_{\mathbf{fgh}} = \frac{1}{N^2} \sum_{\mathbf{kq}} \frac{1}{\mu_{\mathbf{k}} \mu_{\mathbf{q}}} \left[\sin\left(\frac{k_x}{2}\right) \sin\left(\frac{q_x}{2}\right) \cos\left(\frac{k_x + q_x}{2}\right) + \sin\left(\frac{k_y}{2}\right) \sin\left(\frac{q_y}{2}\right) \cos\left(\frac{k_y + q_y}{2}\right) \right] e^{-i\mathbf{k}(\mathbf{f}-\mathbf{g})} e^{-i\mathbf{q}(\mathbf{g}-\mathbf{h})}$$

Values of coefficients Ψ_{fghl} and Φ_{fgh} strongly decrease with increasing distance between sites f, g, h [11], therefore we consider only the intracluster Coulomb interactions, $\Psi_{0000} = 0.2109$, $\Phi_{000} = 0.918$. Now Hamiltonian (6) can be divided into the intracluster and intercluster parts of the interactions:

$$\begin{aligned} H &= H_c + H_{cc} \\ H_c &= \sum_f H_f \\ H_{cc} &= \sum_{fg} H_{fg} \end{aligned} \tag{7}$$

The exact diagonalization of Hamiltonian H_c gives eigenstates and eigenvalues of CuO_6 cluster with hole numbers $n_h = 0,1,2$. Hole vacuum ($n_h = 0$) eigenstates are just the harmonic oscillator states:

$$|0,\nu\rangle = |0\rangle\,|\nu\rangle,\ \nu = 0,1,...,N_{\max} \tag{8}$$

Here $|0\rangle$ denotes electronic configuration $\left|3d^{10}2p^6\right\rangle$. Phonon states $\left|\nu\right\rangle$ are ν-times action of phonon creation operator $A^{\dagger}$ on vacuum state $\left|0,0,...,0\right\rangle$ of harmonic oscillator:

$$\left|\nu\right\rangle = \frac{1}{\sqrt{\nu!}} \left(A^{\dagger}\right)^{\nu} \left|0,0,...,0\right\rangle \tag{9}$$

In the numerical calculations cutoff $N_{\max}$ for number of phonons in the basis is determined for each given set of parameters from the condition: electron spectral function in the investigated energy region does not change with addition of extra phonons in the basis. At constant diagonal EPI $\lambda_d = 0.3$ and constant off-diagonal EPI $\lambda_{pd} = 0.2$ cutoff is $N_{\max} = 400$ phonons.

The single-hole ($n_h = 1$) cluster eigenstate i has the form of superposition of products of hole and phonon wave functions

$$|1\sigma, i\rangle = \sum_{\nu=0}^{N} \left(c_{i\nu}^{d} |d_\sigma\rangle |\nu\rangle + c_{i\nu}^{b} |b_\sigma\rangle |\nu\rangle \right) \tag{10}$$

where $|d_\sigma\rangle = d^{\dagger}_{x^2-y^2\sigma}|0\rangle$ and $|b_\sigma\rangle = b^{\dagger}_{\sigma}|0\rangle$ are single-hole basis states which correspond to electronic configurations $|3d^9 2p^6\rangle$ and $|3d^{10} 2p^5\rangle$ of stoichiometric La_2CuO_4. Ground single-hole cluster eigenstate ($i = 0$) and four excited eigenstates $i = 1,2,3,4$ are shown in Fig.1(a) for diagonal EPI $\lambda_d = 0.3$ and off-diagonal EPI $\lambda_{pd} = 0.2$. Ground state is dome-like distribution of hole density over multiphonon states $|\nu\rangle$ with maximum at $\nu = 12-13$. Structure of excited states is more complex, there are several maxima in the phonon cloud, the number of maxima is the index of eigenstate i plus one. Average number of phonons in the cloud and phonon states with maximal hole density is less than in regime of only diagonal EPI since diagonal and off-diagonal EPI partially compensate each other.

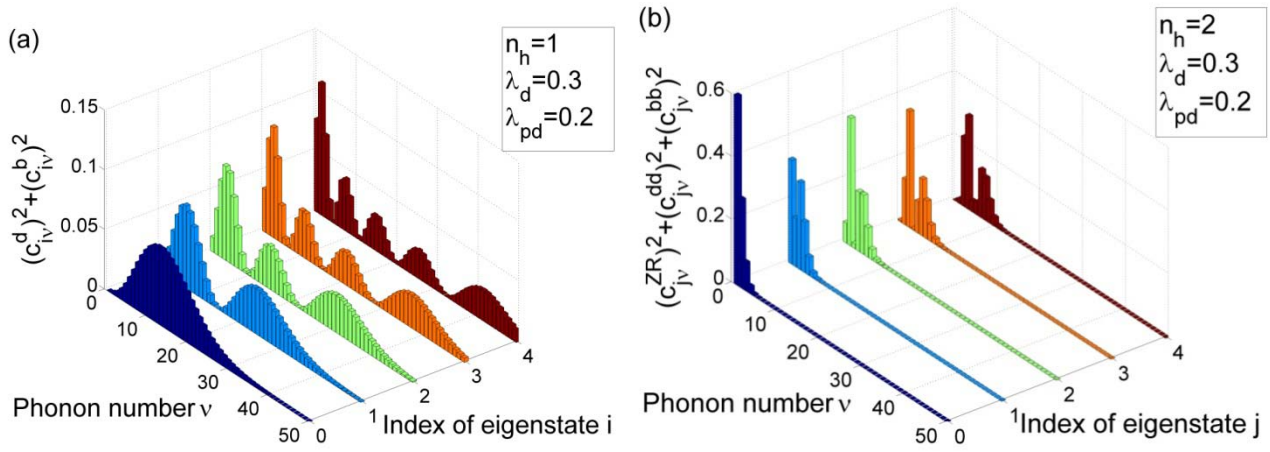

Fig. 1 Structure of the ground and four excited cluster eigenstates for hole number $n_h = 1$ (a) and $n_h = 2$ (b) at diagonal EPI $\lambda_d = 0.3$ and off-diagonal EPI $\lambda_{pd} = 0.2$. Polaronic effect is stronger in single-hole cluster than in two-hole cluster.

Electron part of the two-hole ($n_h = 2$) basis consists of the Zhang-Rice singlet state $|\mathrm{ZR}\rangle = \left| \frac{1}{\sqrt{2}} \left(d_\downarrow b_\uparrow - d_\uparrow b_\downarrow \right) \right\rangle$, the two holes on copper ion state $|d_\downarrow d_\uparrow\rangle$ and the two holes on oxygen ion state $|b_\downarrow b_\uparrow\rangle$.The electronic configurations $|3d^9 2p^5\rangle$, $|3d^8 2p^6\rangle$, $|3d^{10} 2p^4\rangle$ correspond to these states. Two-hole eigenstates of CuO_6 cluster with phonons are also superpositions of products of hole and phonon wave functions:

$$|2, j\rangle = \sum_{\nu=0}^{N} \left(c_{j\nu}^{ZR} |\mathrm{ZR}\rangle |\nu\rangle + c_{j\nu}^{dd} |d_{x\downarrow} d_{x\uparrow}\rangle |\nu\rangle + c_{j\nu}^{bb} |b_\downarrow b_\uparrow\rangle |\nu\rangle \right) \tag{11}$$

Compensation of diagonal and off-diagonal EPI is larger than for single-hole state because of large hole density on oxygen orbitals for two-hole eigenstates which is consequence of strong Coulomb repulsion of two holes on copper orbital. Therefore phonon clouds of two-hole eigenstates have small size (Fig. 1(b)). The main probability in the ground

two-hole cluster eigenstate is at phonon basis state $|0\rangle$. Polaronic effect is weakly manifested in the cluster with two holes compared with single-hole cluster at the same parameters.

Single electron excitations between cluster multielectron eigenstates with N and $N+1$ fermions are described by the Hubbard operators $X_f^{pq} = |p\rangle\langle q|$, where $|q\rangle$ is the initial cluster eigenstate and $|p\rangle$ is the final cluster eigenstate. The Fermi-type operators of annihilation of hole on copper and oxygen orbital can be expressed in terms of the Fermi-type Hubbard operators X_f^{pq}:

$$\begin{aligned} d_{f\sigma} &= \sum_{pq} \gamma_{d\sigma}(pq) X_f^{pq} \\ b_{f\sigma} &= \sum_{pq} \gamma_{b\sigma}(pq) X_f^{pq} \end{aligned} \tag{12}$$

Without EPI the Hubbard operators describe Hubbard fermions. The excitations between eigenstates $|1,i\rangle$ and $|0,\nu\rangle$ form the upper Hubbard band (UHB) of electrons, excitations between cluster eigenstates $|1,i\rangle$ and $|2,j\rangle$ form the lower Hubbard band (LHB) of electrons that is the valence band of the charge transfer insulator in our model. Overlap between multielectron (multihole) polaron states with different average number of phonons is nonzero. Such excitations between polaron states are Franck-Condon processes. Excitations between multielectron polaron states change number of fermions and number of phonons therefore these are polaron excitations. We call them the Hubbard polarons. Intensity (spectral weight) of Hubbard polarons depends on matrix elements and filling of local eigenstates. Occupation of zero- and two-hole eigenstates is zero without doping. Filling of single-hole states and its dependence on temperature are determined by Boltzmann distribution:

$$n_{1i} = n_{10} \exp\left(-\frac{\varepsilon_{1i} - \varepsilon_{10}}{kT}\right) \tag{13}$$

where ε_{1i} is the energy of cluster single-hole eigenstate i. At $T = 0$ K only the ground single-hole state is occupied and only excitations involving the single-hole ground state $|1,0\rangle$ have a non-zero spectral weight. Filling of ground state falls whereas occupation of 1th, 2th and 3rd excited single-hole states grows with increasing temperature, new Hubbard polarons involving occupied single-hole excited states acquire spectral weight.

Hamiltonian of the original model is exactly converted to the multiband Hubbard model within the GTB-method. Hamiltonians H_c and H_{cc} in (7) are rewritten in the terms of Hubbard operators:

$$\begin{aligned} H_c &= \sum_{\mathbf{f}} \left[\sum_l \varepsilon_{0l} X_{\mathbf{f}}^{0l,0l} + \sum_i \varepsilon_{1i} X_{\mathbf{f}}^{1i,1i} + \sum_j \varepsilon_{2j} X_{\mathbf{f}}^{2j,2j} \right] \\ H_{cc} &= \sum_{\mathbf{f}\neq\mathbf{g}} \left[\sum_{mn} 2t_{pd} \mu_{\mathbf{fg}} \gamma_{d_x}^*(m) \gamma_b(n) X_{\mathbf{f}}^{m\dagger} X_{\mathbf{g}}^n - \sum_{mn} 2t_{pp} \nu_{\mathbf{fg}} \gamma_b^*(m) \gamma_b(n) X_{\mathbf{f}}^{m\dagger} X_{\mathbf{g}}^n \right] \end{aligned} \tag{14}$$

Here ε_{0l}, ε_{2j} are the energies of cluster eigenstates with $n_h = 0, 2$. The intercluster interactions includes the p-d and p-p hoppings of the Hubbard polarons between clusters. The matrix of intercluster hopping $\hat{\tilde{t}}(k;\omega)$ contains the matrix elements $\tilde{t}_{\mathbf{k}}^{mn} = \sum_{\lambda\lambda'} \gamma_\lambda^*(m) \gamma_{\lambda'}(n) \tilde{t}_{\mathbf{k}}^{\lambda\lambda'}$. To obtain the band dispersion and spectral function of Hubbard polarons we use the equation of motion for the Green function $D_{mn}(\mathbf{f},\mathbf{g}) = \langle\langle X_{\mathbf{f}}^m | X_{\mathbf{g}}^n \rangle\rangle$, where m,n are the quasiparticle band indexes, this index is uniquely defined by initial and final states of excitation $m \equiv (p,q)$. The electron Green function $G_{\lambda\lambda'}(\mathbf{f},\mathbf{g}) = \langle\langle a_{\lambda\mathbf{f}} | a_{\lambda'\mathbf{g}}^\dagger \rangle\rangle$ is determined by the quasiparticle Green function $D_{mn}(\mathbf{f},\mathbf{g})$ from the following relation:

$$G_{\lambda\lambda'}(\mathbf{f},\mathbf{g}) = \sum_{mn} \gamma_{\lambda'}^*(n) \gamma_\lambda(m) D_{mn}(\mathbf{f},\mathbf{g}) \tag{15}$$

There are many quasiparticle excitations in our system therefore it is convenient to introduce matrix Green function $\hat{D}(\mathbf{f},\mathbf{g})$ with matrix elements $D_{mn}(\mathbf{f},\mathbf{g})$, indexes of row m and column n run over all quasiparticle bands. The set of equations of motion is decoupled in the generalized Hartri-Fock approximation by method of irreducible Green functions [12-15] taking into account the interatomic spin-spin correlation functions. The Dyson equation for the matrix Green function $\hat{D}(f,g)$ in the momentum space has the form

$$\hat{D}(\mathbf{k};\omega)=\left[\hat{D}_0^{-1}(\omega)-\hat{F}\hat{\hat{t}}(\mathbf{k};\omega)+\hat{\Sigma}(\mathbf{k};\omega)\right]^{-1}\hat{F} \tag{16}$$

In this equation $\hat{D}_0$ is the exact local Green function, its matrix elements $D_0^{mn}=\dfrac{\delta_{mn}F(m)}{\omega-\Omega(m)}$, $\Omega(m)=\Omega(pq)=E_p-E_q$ is the energy of the quasiparticle local excitation between states q and p, $F(m,n)=F(m)\delta_{mn}$, $F(m)=F(pq)=\langle X^{pp}\rangle+\langle X^{qq}\rangle$ is the filling factor of the quasiparticle. $\hat{\Sigma}(\mathbf{k};\omega)$ is the self-energy operator which contains spin-spin correlation functions. Result of applying GTB method is presentation of electronic spectra as spectra of quasiparticle excitations constructed out of the local states of the cluster. At zero temperature the band structure of Hubbard polarons has been discussed for different sets of the diagonal and off-diagonal EPI couplings in [16,17].

4. TEMPERATURE DEPENDENCE OF THE ELECTRON SPECTRAL FUNCTION IN THE SYSTEM WITH DIAGONAL AND OFF-DIAGONAL EPI FOR BREATHING LOCAL OXYGEN MODE.

Low-energy band structure of pure electronic system without phonons and EPI within two-band Hubbard model is LHB and UHB, bands of Hubbard fermions. Spectral function of LHB is high-intensity coherent quasiparticle peak. Band structure without EPI at $T=0$ K is two Hubbard bands plus number of dispersionless degenerate Franck-Condon resonances between cluster vibronic levels with zero spectral weight, some of them crossing the Hubbards bands. Lower Hubbard band is formed by excitation between single-hole and two-hole ground vibronic states with zero phonons (which is called 0-0 Franck-Condon resonance). Franck-Condon resonances are formed by multiphonon excitations between multiphonon vibronic levels. Spectral function of LHB remains the same as in pure electronic system since peaks of multiphonon excitations have zero spectral weight without EPI. The EPI results in hybridization of the Hubbard bands and local Franck-Condon resonances. Multiphonon polaron excitations acquire spectral weight and dispersion. Hubbard band is split into a multiplet of polaron subbands (Fig.2(a)). Intensity of spectral function peaks of multiphonon excitations becomes non zero. At large EPI spectral weight of high-intensity coherent quasiparticle peak is transferred to peaks that originate from multiphonon excitations (Fig.3, line for $\delta=0.001$ eV). Taking into account finite lifetime of quasiparticles leads to formation of one wide peak (Fig.3, black line for $\delta=0.03$ eV).

Several tendencies in modification of electronic structure with increasing temperature can be distinguished. At first valence band is reconstructed: the band is split off from the rest of band, the top subband reverts with the temperature increasing, global maximum at point $\mathbf{k}=(\pi/2,\pi/2)$ becomes local minimum and maximum energy of band is at points $\mathbf{k}=(0,0)$ and $\mathbf{k}=(\pi,\pi)$ (Fig.2(b)). Secondly number of splittings into polaron subbands grows, and LHB gets more blurred (Fig.2(b)). Third, the spectral weight is redistributed due to new polaron excitations that acquire spectral weight with thermal filling of excited single-hole local polaron states. Also spectral weight is redistributed over large number of points in the k-space and its distribution is more homogeneous, i.e. the original dispersion of three-band p-d model is lost.

New multiphonon peaks is added to spectral function of Hubbard polarons

$$A(\mathbf{k},\omega)=\left(-\frac{1}{\pi}\right)\sum_{\lambda\lambda' mn}\gamma^{*}_{\lambda'}(n)\gamma_{\lambda}(m)\,\mathrm{Im}\left\langle\left\langle X^{m}_{\mathbf{k}}\middle| X^{n}_{\mathbf{k}}\right\rangle\right\rangle_{\omega+i\delta} \tag{17}$$

the most intensive peak losses spectral weight and its satellites acquire intensity with temperature increasing (Fig.3, red line for $\delta = 0.001$ eV). It is seen that at $T = 400$ K spectral function at line width $\delta = 0.03$ eV, envelope of multiphonon peaks, it is broadened by approximately 1.6 times compared with the spectral function at $T = 0$ K. At $T = 0$ K full width at half maximum $\Gamma_{FWHM} = 0.14$ eV whereas at $T = 400$ K $\Gamma_{FWHM} = 0.22$ eV. Maximal intensity of broad peak falls with temperature increasing. These results are in qualitative agreement with broadening obtained from ARPES spectra [2,3].

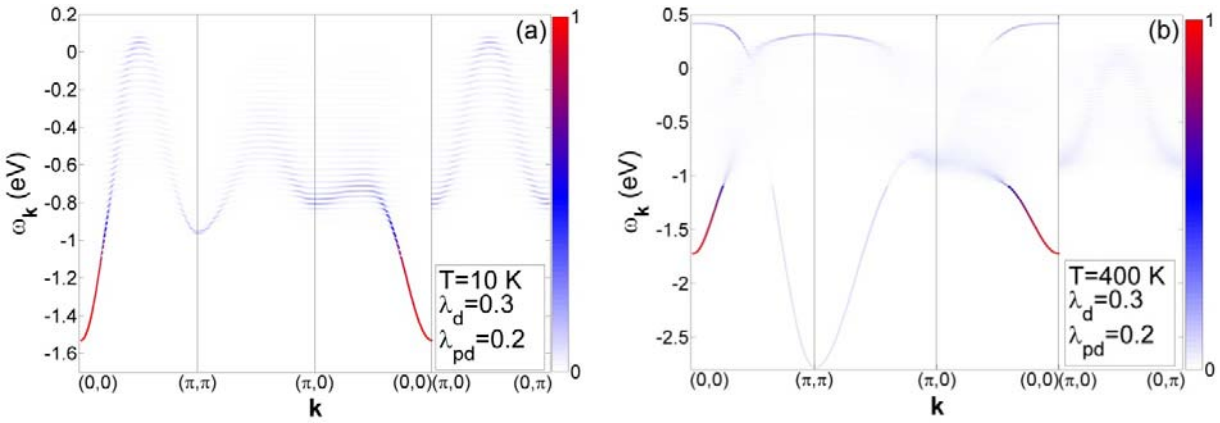

Fig. 2 Evolution of the valence band structure with increasing temperature at diagonal EPI $\lambda_d = 0.3$ and off-diagonal EPI $\lambda_{pd} = 0.2$. (a) Band structure with spectral weight of quasiparticles in each k-point (spectral weight is displayed by color) at (a) $T = 10$ K, (b) $T = 400$ K, only the valence band region of energies is shown because the spectral weight of the conductivity band is strongly suppressed at high temperature.

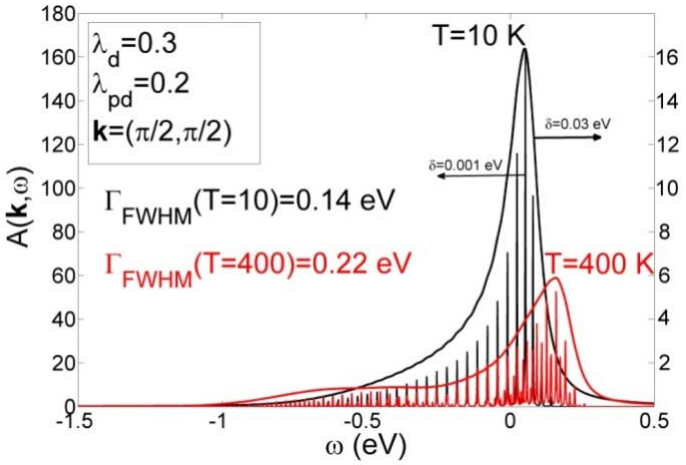

Fig.3 The evolution of the electron spectral function at $\mathbf{k} = \left(\frac{\pi}{2}, \frac{\pi}{2}\right)$ with increasing temperature at diagonal EPI $\lambda_d = 0.3$ and off-diagonal EPI $\lambda_{pd} = 0.2$. Black lines show spectral functions at $T = 10$ K, red lines show spectral functions at $T = 400$ K. Axis of intensity on the left is related to line width $\delta = 0.001$ eV, axis of intensity on the right is related to $\delta = 0.03$ eV. Many narrow peaks are formed by multiphonon Franck-Condon excitations, that is evident at $\delta = 0.001$ eV. At $\delta = 0.03$ eV multiphonon peaks merge into a single broad peak. FWHM of the spectral function at $T = 400$ K ($\Gamma_{FWHM}(T = 400) = 0.22$ eV) is larger by 1.6 times than at $T = 10$ K ($\Gamma_{FWHM}(T = 10) = 0.14$ eV).

5. DEPENDENCE OF ELECTRON SPECTRAL FUNCTION ON MAGNITUDE OF DIAGONAL EPI FOR BREATHING AND BUCKLING LOCAL OXYGEN MODES.

Usually simplified models are restricted to include a single phonon mode, while in a crystal the number of phonon modes is large. In this chapter we model the effect of several modes EPI on the polaronic spectral weight by considering two phonon modes model. All calculations are similar to the previous case, and for simplicity we restricted to the main contribution to the spectral function given by the intracluster excitations. Thus we neglect the dispersion of polaron at the top of the valence band. It is clear from Fig.2b that at the elevated temperatures the dispersion is negligible, justifying our approximation. The polaronic spectral function for breathing and buckling modes is shown in Fig.4. Presence of two modes results in appearance of second peak in the spectral function at weak EPI. We consider regime of equal constants of EPI with breathing and buckling modes, $\lambda_d = \lambda_a = \lambda$. The EPI increasing leads to substantial broadening of the hole spectral function (Fig.4).

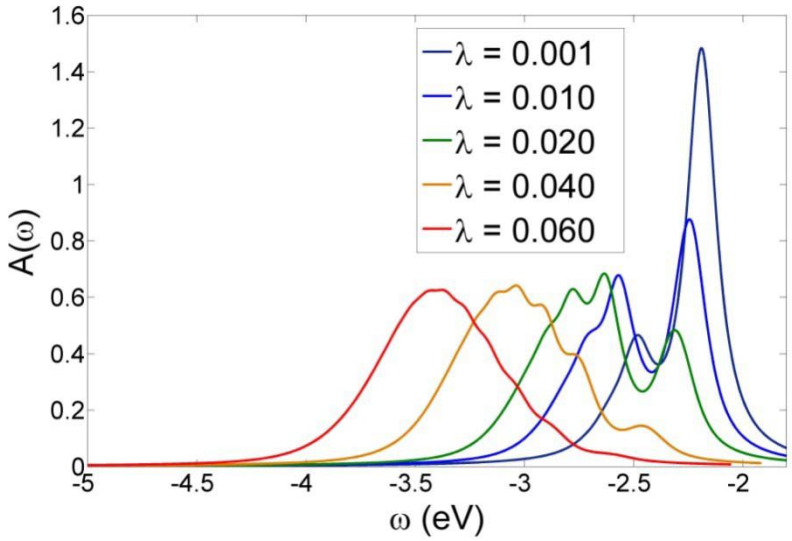

Fig.4 The evolution of the hole spectral function of dispersionless quasiparticles of conductivity band with increasing diagonal EPI, EPI with breathing and buckling modes are equal i.e. $\lambda_d = \lambda_a = \lambda$.

6. CONCLUSION

Electronic spectra of undoped cuprates are characterized by a wide LHB peak and show strong temperature dependence. Both features are described by polaronic origin of quasiparticle excitations in these compounds within polaronic GTB method. Broad peak is formed by a large number of multiphonon excitations peaks. EPI with two phonon modes enhances this effect and broadening is manifested even at small and moderate EPI constants. Filling of local polaronic states with increasing temperature results in substantial redistribution of the spectral weight among polaronic multiphonon excitations and reconstruction of band structure. The main consequences of these transformations are spectral function broadening and damping of maximal intensity of wide peak with increasing temperature.

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