METALS
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Effect of Pressure on the Electronic Structure of Cuprates with Strongly Correlated Electrons

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Abstract—For cuprates of the *n* and *p* types, the effect of pressure on the electronic structure of a CuO_2 layer is studied. In the calculations performed, a generalized tight-binding method is used taking into account the influence of strong electronic correlations on the electronic structure of cuprates. The results obtained demonstrate the unusual effect of pressure on the nature of quasiparticle states at the top of the valence band in *p*-type cuprates. As the pressure increases, the hole states in these materials cease to be Zhang–Rice singlets and become combined singlet–triplet states.

1. INTRODUCTION

It is well known that pressure has a great effect on the properties of high-temperature superconductors, especially on the value of T_c [1, 2]. This pressure effect greatly exceeds the analogous effect observed for ordinary metallic superconductors. The characteristic feature of this effect is that the temperature T_c of the transition to a superconducting state depends strongly on the doping level. It is remarkable that, if pressure is applied to a lightly doped sample whose transition temperature $T_c = T_{ci}$ without pressure is less than T_{cm} (the maximum temperature that can be reached under optimal doping conditions), then the superconducting transition temperature can exceed T_{cm}. For example, the Tl-2223 superconductor has $T_{cm} = 125$ K at atmospheric pressure. External pressure affects this parameter only slightly. However, pressure applied to a lightly doped sample with $T_c = T_{ci} = 116$ K increases this parameter up to $T_c = T_{cp} = 132$ K, which exceeds T_{cm}. The pressure effect is not universal for cuprates. For example, the pressure dependence of T_c is very weak for the $Nd_{1.85}Ce_{0.15}CuO_{4-x}$ compound, which likewise contains a CuO_2 layer.

The electronic structure of high-temperature superconducting materials changes under an applied pressure. The results of photoemission studies of the insulating $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ compounds ($0.92 < x < 0.55$) [3] demonstrate indirectly that applying pressure to cuprates has unusual consequences. Specifically, the "chemical pressure" (which arises when Y substitutes for Ga) manifests itself in an unexpectedly strong change in the shape of the dispersion relation of carriers at the top of the valence band.

The aim of this paper is to theoretically study the pressure effect on the electronic structure of the CuO_2 layers in *n*- and *p*-type materials. The Nd_2CuO_4 (NCO) and La_2CuO_4 (LCO) compounds are considered. To take into account strong electron correlations in the electronic structure of these compounds, a calculation is carried out in the framework of the generalized tight-binding (GTB) method [4, 5].

2. ELECTRONIC STRUCTURE

The calculation scheme used to find the electronic structure of NCO and LCO was given in detail in [4, 5]. For this reason, we discuss only its key points in this paper. The NCO and LCO unit cells are shown in Fig. 1. Let us consider the case where pressure is applied along the *c* axis of the crystal; i.e., the point symmetry group D_{4h} of the oxygen octahedron remains unchanged. Hydrostatic pressure or uniform pressure applied in the plane normal to the *c* axis does not lead to any interesting effects in our calculations. Pressure is taken into account by introducing an appropriate parameter into the intracluster hopping integrals

$$t_{pd}(P) = t_{pd}(0) - \alpha_1 P, \quad t_{pp}(P) = t_{pp}(0) - \alpha_2 P,$$

$$t_{pd}^{ap}(P) = t_{pd}^{ap}(0) + \alpha_3 P, \quad t_{pp}^{ap}(P) = t_{pp}^{ap}(0) + \alpha_4 P,$$

where t_{pd} is the hopping integral between the central copper atom of an oxygen octahedron and an in-plane oxygen atom, t_{pp} is the hopping integral between in-plane oxygen atoms, and t_{pd}^{ap} and t_{pp}^{ap} are the respective hopping integrals related to an apical oxygen atom. The one-hole energies ε_{dx}, ε_{dz}, and ε_p and the hopping inte-

grals t_{pd}, t_{pp}, t_{pd}^{ap}, and t_{pp}^{ap}, as well as the Coulomb interaction parameters, are calculated using the ab initio local density approximation (LDA) method [6]. From general considerations, it is clear that all the parameters α are of the same order. For this reason, we assume that $\alpha_1 = \alpha_2 = \alpha_3 = \alpha_4 = \alpha = 0.0005$ eV/GPa in order to simplify our calculations. The value of α is taken from [7], where it was calculated by the LDA method for $FeBO_3$.

3. SHORT DESCRIPTION OF THE GENERALIZED TIGHT-BINDING METHOD

Using the GTB method, the Hamiltonian for a CuO_2 layer can be written in the form [8]

$$H = \sum_{i\lambda\sigma} \varepsilon_i^\lambda \alpha_{i\lambda\sigma}^+ \alpha_{i\lambda\sigma}$$

$$+ \sum_{i,j} \sum_{\lambda_1\lambda_2\sigma_1\sigma_2\sigma_3\sigma_4} V_{ij}^{\lambda_1\lambda_2} \alpha_{i\lambda_1\sigma_1}^+ \alpha_{i\lambda_1\sigma_3} \alpha_{i\lambda_2\sigma_2}^+ \alpha_{j\lambda_2\sigma_4} \quad (1)$$

$$+ \sum_{\langle i,j \rangle} \sum_{\lambda_1\lambda_2\sigma} t_{ij}^{\lambda_1\lambda_2} a_{i\lambda_1\sigma}^+ a_{j\lambda_2\sigma}.$$

Here, $a_{i\lambda\sigma}$ is the annihilation operator for a hole at site i (copper or oxygen) in orbital λ with spin σ. We take into account two copper orbitals ($d_{x^2-y^2}$) and d_{z^2}) and the oxygen p_x, p_y, and p_z orbitals (at each oxygen site) forming σ bonds with the above-mentioned copper orbitals. Among the Coulomb matrix elements, one can single out the intra-atomic Hubbard matrix elements U_d (U_p) for the repulsion of two holes with opposite spins on the same copper (oxygen) orbital; the interorbital Coulomb V_d (V_p) and exchange J_d (J_p) matrix elements; and the interatomic Coulomb repulsion parameters V_{pd}, which, for simplicity, are assumed to be the same for all orbitals. The last term in Eq. (1) describes interatomic copper–oxygen hopping with parameters $t_{pd}^{x^2-y^2,x(y)} \equiv t_{pd}$ and $t_{pd}^{z^2,x} \equiv t_{pd}/\sqrt{3}$ and oxygen–oxygen hopping with parameter $t_{pp}^{x,y} \equiv t_{pp}$. Of the six oxygen ions, two apical ions are located on the c axis in the T structure of the LCO composition. In our calculations, the contributions from these two ions are described by two parameters, namely, the t_{pd}' and t_{pp}' hopping integrals from copper and in-plane oxygen, respectively, to an apical oxygen.

In the GTB method, the band structure of quasiparticles with the inclusion of strong electron correlations is calculated in two steps. At the first step, the CuO_2-layer lattice is divided into a set of unit cells and the intracell part of the Hamiltonian is diagonalized exactly. A CuO_6 cluster is chosen as the unit cell, and
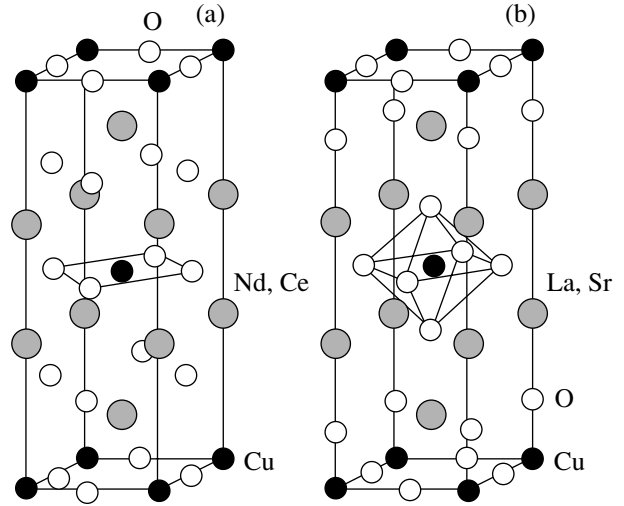

Fig. 1. Unit cells of (a) Nd_2CuO_4 and (b) La_2CuO_4.

b_{1g}- and a_{1g}-symmetry Wannier functions are constructed using the initial oxygen orbitals [4]. The many-electron molecular orbitals $|n, p\rangle$ obtained by diagonalizing the Hamiltonian H_0 of the unit cell ($n = 0, 1, 2 \ldots$ is the number of holes in the cell, and p stands for the set of other orbital and spin indices) are used to construct the Hubbard operators $X^m = |n + 1, p\rangle\langle n, q|$ for this cell and one-electron operators $a_{f\lambda\sigma} = \sum_m \gamma_{\lambda\sigma}(m) X_{f\sigma}^m$. Here, the quasiparticle band index m enumerates one-electron excitations of the initial states $|n, q\rangle$ to the final states $|n + 1, p\rangle$ of the quasiparticles.

In the GTB method, the dispersion relations and the spectral density can be written in the form [8]

$$\left\| (E - \Omega_m^G)\delta_{mn}/F_\sigma^G(m) - 2\sum_{\lambda\lambda'} \gamma_{\lambda\sigma}^*(m) T_{\lambda\lambda'}^{PG}(\mathbf{k})\gamma_{\lambda'\sigma}(n) \right\| \quad (2)$$
$$= 0,$$

$$A_\sigma(\mathbf{k}, E) = \left(-\frac{1}{\pi}\right)\sum_\lambda \mathrm{Im}(G_{\mathbf{k},\sigma}^{\lambda\lambda})$$

$$= \left(-\frac{1}{\pi}\right)\sum_{\lambda mn} \gamma_{\lambda\sigma}(m)\gamma_{\lambda\sigma}^+(n)\mathrm{Im}(D_{\mathbf{k}\sigma}^{mn}(AA) + D_{\mathbf{k}\sigma}^{mn}(BB)), \quad (3)$$

where

$$G_{\mathbf{k}\sigma}^{\lambda\lambda'} = \langle\langle a_{\mathbf{k}\lambda\sigma}|a_{\mathbf{k}\lambda'\sigma}^+\rangle\rangle_E = \sum_{mn} \gamma_{\lambda\sigma}(m)\gamma_{\lambda'\sigma}^+(n)D_{\mathbf{k}\sigma}^{nm}, \quad (4)$$

$$\hat{D}_{\mathbf{k}\sigma} = \begin{pmatrix} \hat{D}_{\mathbf{k}\sigma}(AA) & \hat{D}_{\mathbf{k}\sigma}(AB) \\ \hat{D}_{\mathbf{k}\sigma}(BA) & \hat{D}_{\mathbf{k}\sigma}(BB) \end{pmatrix}, \quad (5)$$

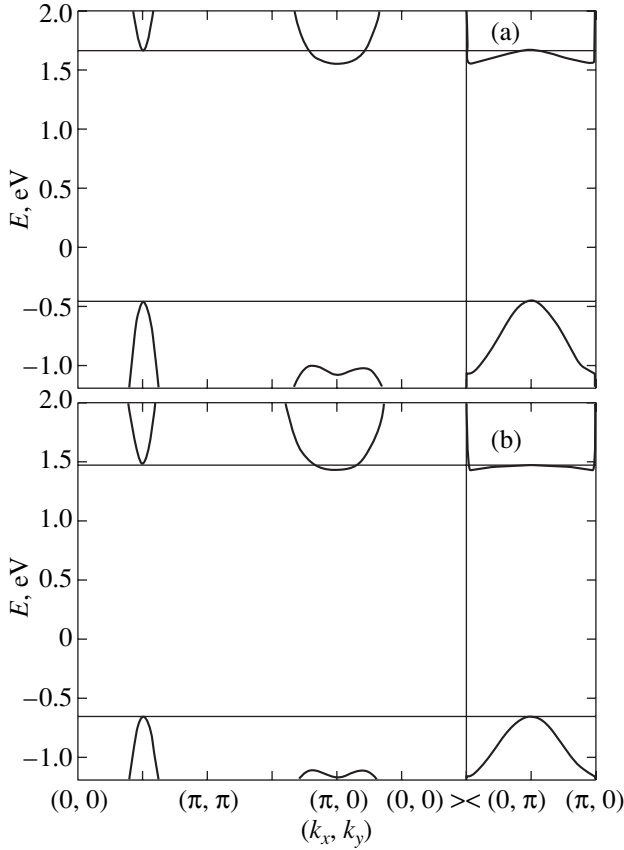$$D_{\mathbf{k}\sigma}^{mn}(AB) = \langle\langle X_{\mathbf{k}\sigma}^m|Y_{\mathbf{k}\sigma}^n\rangle\rangle_E.$$

Fig. 2. Band structure of Nd$_2$CuO$_4$ (a) at zero pressure and (b) at a pressure of 150 GPa.

Fig. 3. Pressure dependences of the quasiparticle energies at symmetry points in the Brillouin zone for Nd$_2$CuO$_4$. The dot-and-dash line corresponds to the point ($\pi/2$, $\pi/2$) of the conduction band, the solid line corresponds to the point (π, 0) of the conduction band, the solid bold line corresponds to the point ($\pi/2$, $\pi/2$) of the valence band, and the dashed line corresponds to the point (π, 0) of the valence band.

Here, the superscripts P and G run through the lattices A and B of the antiferromagnetic state. Equations (2) and (3) are obtained for the antiferromagnetic phase [4]

using the equations of motions for the Green's functions (5) in the Hubbard approximation for intercell hopping. Using a five-orbital basis (d_x, d_z, b, a, p_z), the elements of the "tight-binding" matrix

$$T_{\lambda\lambda'}^{AA}(\mathbf{k}) = T_{\lambda\lambda'}^{BB}(\mathbf{k}) = \frac{2}{N}\sum_{\mathbf{R}_1} T_{\lambda\lambda'}^{AA}(\mathbf{R}_1)\exp(i\mathbf{k}\mathbf{R}_1),$$

$$T_{\lambda\lambda'}^{AB}(\mathbf{k}) = T_{\lambda\lambda'}^{BA}(\mathbf{k}) = \frac{2}{N}\sum_{\mathbf{R}_2} T_{\lambda\lambda'}^{AB}(\mathbf{R}_2)\exp(i\mathbf{k}\mathbf{R}_2)$$

can be written as

$$T_{\lambda\lambda'}(\mathbf{R}) = \begin{pmatrix} 0 & 0 & -2t_{pd}\mu_{ij} & 0 & 0 \\ 0 & 0 & 2t_{pd}\xi_{ij}/\sqrt{3} & 2t_{pd}\lambda_{ij}/\sqrt{3} & 0 \\ -2t_{pd}\mu_{ij} & 2t_{pd}\xi_{ij}/\sqrt{3} & -2t_{pp}\nu_{ij} & 2t_{pp}\chi_{ij} & -2t'_{pp}\xi_{ij} \\ 0 & 2t_{pd}\lambda_{ij}/\sqrt{3} & 2t_{pp}\chi_{ij} & 2t_{pp}\nu_{ij} & -2t'_{pp}\lambda_{ij} \\ 0 & 0 & -2t'_{pp}\xi_{ij} & -2t'_{pp}\lambda_{ij} & 0 \end{pmatrix}, \qquad (6)$$

where the coefficients μ_{ij}, ξ_{ij}, λ_{ij}, ν_{ij}, and χ_{ij} can be found in [4]. Equation (2) is an analog of the dispersion equation in the tight-binding method, but it differs from this equation in two ways. First, the quasiparticle energies are calculated in the form $\Omega_m^G = \varepsilon_{2qG} - \varepsilon_{1pG}$ (resonances between multiparticle states from different sectors of the configuration space). Second, the occupation
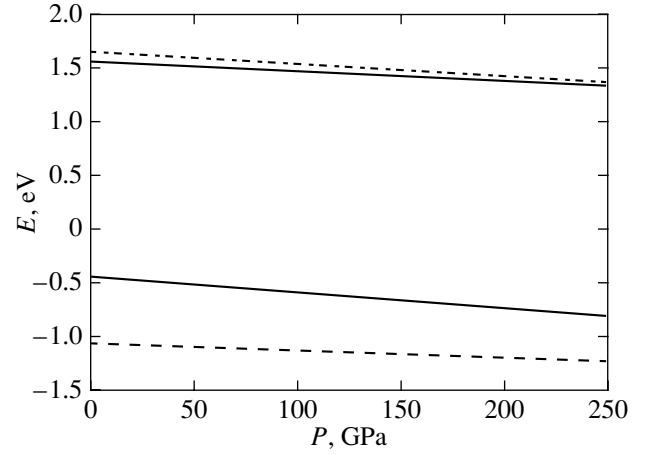
factor $F_\sigma^G(m) = \langle X_{f_G\sigma}^{pp}\rangle + \langle X_{f_G\sigma}^{qq}\rangle$ leads to concentration dependences of both the dispersion and the amplitude of the spectral density (3). Quasiparticle states with different values of m can overlap and interact with each other just as in the case of singlet (A_{1g}) and triplet ($^3B_{1g}$) two-hole states in p-type cuprates [4].
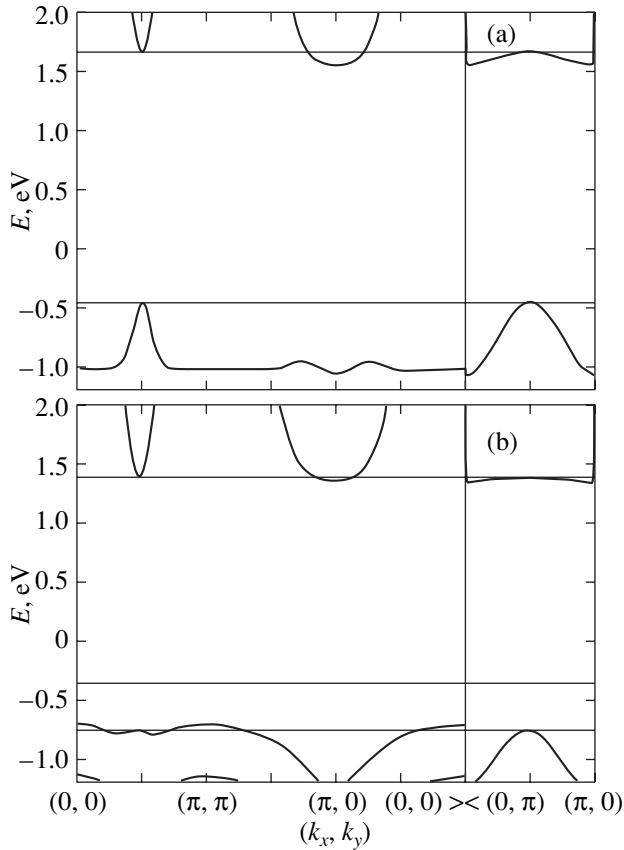
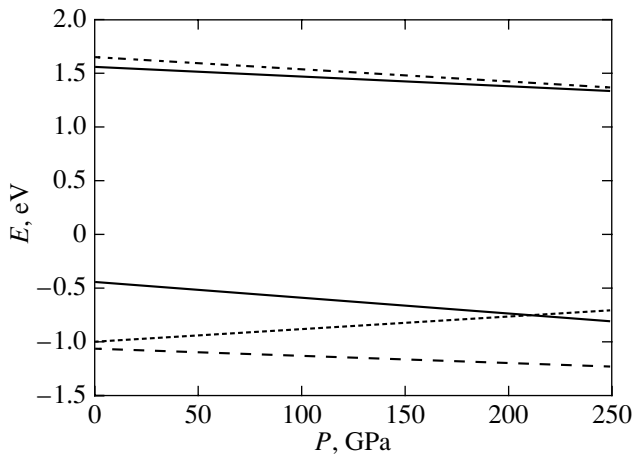**Fig. 4.** Band structure of La_2CuO_4 (a) at zero pressure and (b) at a pressure of 220 GPa.

Fig. 5. Pressure dependences of the quasiparticle energies at symmetry points in the Brillouin zone for La_2CuO_4. The dot-and-dash line corresponds to the point $(\pi/2, \pi/2)$ of the conduction band, the solid line corresponds to the point $(\pi, 0)$ of the conduction band, the solid bold line corresponds to the point $(\pi/2, \pi/2)$ of the valence band, the dotted line corresponds to the points $(0, 0)$ and (π, π) of the valence band, and the dashed line corresponds to the point $(\pi, 0)$ of the valence band.

4. CALCULATION RESULTS

Figure 2 shows the NCO band structure at zero pressure and at 150 GPa. At zero pressure, the results coincide with those obtained in [6]. It is seen that the changes in the NCO band structure are quantitative in character. Figure 3 demonstrates the pressure dependence of the quasiparticle energies at symmetry points in the Brillouin zone. The dielectric gap narrows.

For the LCO, the situation is more complicated, as seen in Fig. 4. At zero pressure, the results obtained in [6] are reproduced. A specific feature of the structure of the valence band calculated using the GTB method is the presence of a singlet and a triplet band. The triplet states at zero pressure are located about 0.5 to 0.7 eV below the valence-band top (Fig. 4a). As the pressure increases, these states move to the top of the valence band (Figs. 4b, 5). As a result, the hole states in these materials become mixed singlet–triplet states.

5. CONCLUSIONS

The difference between the pressure dependences of the NCO and LCO band structures is important for understanding the reasons for the different dependences of the critical temperatures of electron and hole high-temperature superconductors. In spite of the fact that a high-pressure superconductivity theory based on our calculations has not yet been constructed, the reason for the different pressure dependences of T_c can be as follows. In n-type cuprates, the band structure undergoes only small shifts of the band extrema; hence, the effective low-energy Hamiltonian has the form of a t–J model with pressure-dependent parameters t and J. In hole cuprates, the shift of triplet states to the top of the valence band changes the effective model noticeably with increasing pressure. The effective Hamiltonian obtained for hole cuprates in the framework of the GTB method is similar to that of the two-band singlet–triplet model [9]. Bose-type singlet–triplet excitations (spin excitons) were proposed in [10, 11] as an additional possible pairing mechanism. However, at zero pressure, the distance between the singlet and triplet bands is fairly large (about 0.5–0.7 eV); so, the contribution of spin excitons is small. As the pressure increases, the distance between these bands decreases (according to our results), which should enhance the spin-exciton pairing mechanism operating additionally to the magnetic mechanism of the t–J model. As a result, the pressure dependence of T_c should become stronger.

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