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# Comparison of the Single-Electron and Many-Electron Mechanisms of the Concentration Dependence of the HTSC Cuprate Band Structure

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**Abstract**—The band structure of the  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  HTSC is calculated using the LDA + GTB method, which combines the local density approximation (LDA) and the generalized tight-binding (GTB) method. Two mechanisms of the concentration dependence of the band structure (single-electron and many-electron mechanisms) are taken into account. It is demonstrated that the main contribution to the evolution of the band structure with doping comes from the many-electron mechanism.

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## 1. INTRODUCTION

It is well known that hole doping of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  and electron doping of  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  turn the Mott–Hubbard insulators  $\text{La}_2\text{CuO}_4$  and  $\text{Nd}_2\text{CuO}_4$  into superconductors. The band structure undergoes massive changes with increasing dopant concentration  $x$ , from the antiferromagnetic (AFM) insulator to a normal paramagnetic metal. Strong electron correlations are a decisive factor in the formation of the electronic structure of HTSC cuprates, especially for small  $x$ , and have to be taken into account. In the present paper, we study the band structure of  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  using the LDA + GTB method [1], which combines a many-electron approach within the generalized tight-binding (GTB) model [2] and ab initio calculations within the local electron density approximation (LDA). Previously, the GTB approach was used to reveal a special many-electron mechanism of the evolution of the band structure of doped Mott–Hubbard insulators; this mechanism involves variations in the filling of many-electron terms between which single-electron quasiparticles are excited [2]. In  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ , such terms are the  $d^{10}p^6$  term (without holes) and a hybrid  $d^9p^6 + d^{10}p^5$  term (one hole per unit cell).

Certainly, there is also a single-electron mechanism of influence of the doping on the band structure, in which the lattice parameters of crystals vary with

increasing  $x$ . As a result, the matrix elements of  $p$ – $d$  hybridization and  $p$ – $p$  hopping and all other that depends on the interatomic distances change with doping level. It is this mechanism that would be responsible for the evolution of the band structure with doping within standard band theory in the absence of strong electron correlations. That is why we call it single-electron.

Until now, there have been no calculations of the band structure of HTSC cuprates with inclusion of both mechanisms. In this paper, we present the results of such calculations for  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  and compare them with the results of a simplified approach where the single-electron mechanism is not taken into account. It turns out that, in the case of weak doping ( $x \leq 0.10$ ), the single-electron mechanism produces only weak quantitative changes (shift of the bottom of the conduction band). However, at  $x = 0.20$  (in the range of the superconducting phase), complete calculations differ from a simplified one to a greater extent and the single-electron mechanism increases in importance.

## 2. BRIEF DESCRIPTION OF THE LDA + GTB METHOD

Ab initio calculations of the electronic structure in terms of density functional theory has been most developed within LDA. This approximation does not take

into account strong electron correlations and, therefore, cannot describe the band structure of Mott insulators adequately. We perform LDA calculations in order to find the matrix elements of the many-electron Hamiltonian in the multiband  $p-d$  model. This Hamiltonian is then used to calculate the electronic structure with inclusion of strong electron correlations within the GTB approach [1]. Thus, the LDA + GTB method consists of the following steps.

(i) Ab initio LDA calculation of the band structure and determination of Bloch functions.

(ii) Construction of Wannier functions.

(iii) Construction of the multiband  $p-d$  model, whose parameters are calculated using the Wannier functions.

(iv) Decomposition of the Hamiltonian of the multiband  $p-d$  model into a sum of intracell and intercell terms and exact diagonalization of the intercell part, which makes it possible to construct many-electron molecular orbitals of the cell.

(v) Construction of intracell Hubbard  $X$  operators in the basis of these orbitals and representation of the total Hamiltonian of the crystal in terms of the  $X$  operators.

(vi) Calculation of the energy band structure of quasiparticles (Hubbard fermions) within perturbation theory with respect to small intercell hopping matrix elements and interactions. We limit ourselves to the Hubbard-1 approximation in the GTB approach, though the diagram technique for  $X$  operators [3] makes it possible to go beyond this approximation.

In the Hubbard-1 approximation, the dispersion equation for the band structure of Hubbard fermions in the AFM phase with sublattices  $P$  and  $G$  corresponding to the ground state of the undoped  $\text{La}_2\text{CuO}_4$  and  $\text{Nd}_2\text{CuO}_4$  is given by [2]

$$\left\| \left( E - \Omega_m^G \right) \delta_{mn} / F_\sigma^G(m) - 2 \sum_{\lambda\lambda'} \gamma_{\lambda\sigma}^*(m) T_{\lambda\lambda}^{PG}(\mathbf{k}) \gamma_{\lambda'\sigma}(n) \right\| = 0, \quad (1)$$

where  $\Omega_m$  is the intracell local energy of a Hubbard fermion,  $m$  is the band index in the  $X$  representation,  $T_{\lambda\lambda'}(k)$  is the Fourier transform of the matrix element of intercell hopping between single-electron orbitals  $\lambda$  and  $\lambda'$ , and  $\gamma_{\lambda\sigma}(m)$  are the parameters of the representation of the single-electron Fermi operator  $a_{i\lambda\sigma}$  in terms of the Hubbard operators  $X_i^m$ . The filling factor  $F_\sigma(m)$  is equal to the sum of the fillings of the initial and final many-electron states, the transition between which is described by the operator  $X_i^m$ . The structure of dispersion relation (1) is similar to that in the single-electron tight-binding approximation, which explains the term “generalized tight-binding” (GTB) method. However, Eq. (1) differs from its single-electron analog in that the local energies  $\Omega_m$  are calculated including strong electron correlations within the cell exactly and that the filling factor can be noninteger and varies with tempera-

ture and doping level. As a result, the band structure cannot be described in terms of the rigid-band model at all; i.e., the effect of doping is not reduced just to a change in the chemical potential in a given band structure. On the contrary, the band structure is dependent on the concentration  $x$  and doping leads to the formation of new bands, whose spectral weight is proportional to  $x$  for small  $x$ . Such bands arise, for example, inside the insulating gap near the bottom of the conduction band in  $n$ -type cuprates and near the top of the valence band in hole-doped cuprates; they were called in-gap states in [2]. These are not impurity levels in a doped semiconductor that are formed in the potential well of a defect, because defects are not taken into account in the  $p-d$  model. An example of in-gap states near the bottom of the conduction band in  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  is discussed in Section 4.

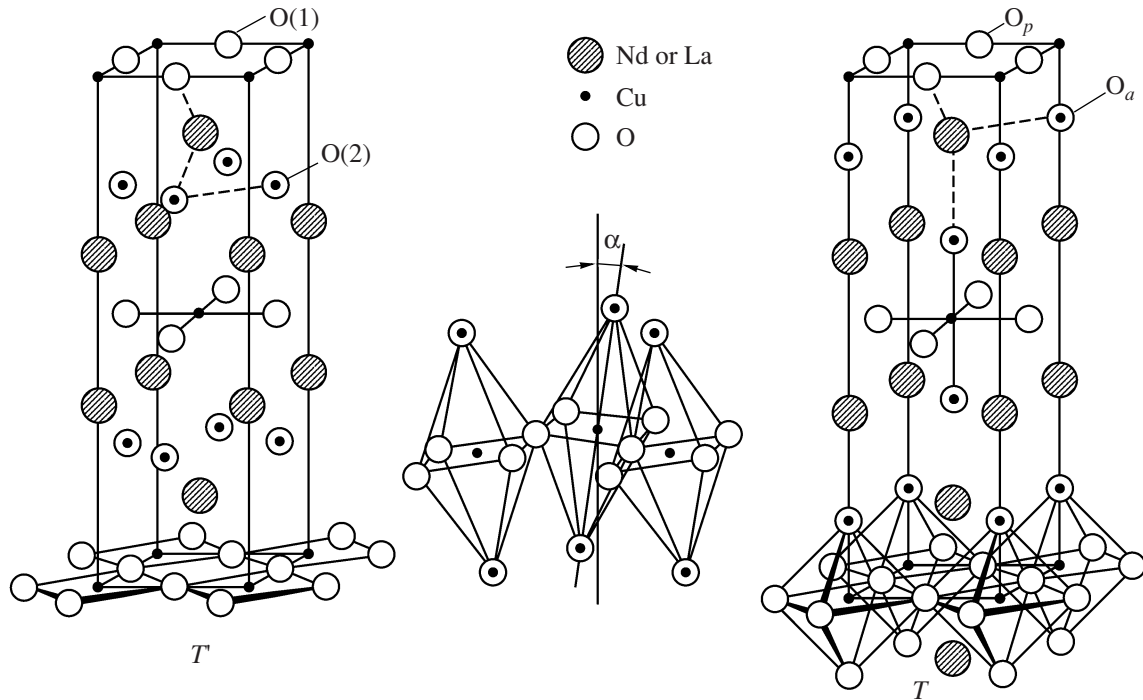
Note that the original version of the GTB method [2] used a large number of unknown parameters of the Hamiltonian, which were obtained by comparing different calculations with experimental data. In the hybrid LDA + GTB method, all parameters are calculated. By specifying concentration  $x$ , we calculate the band structure for any value of  $x$ . The many-electron mechanism of the dependence of the band structure on doping level arises because the filling factor depends on  $x$ . The single-electron mechanism of this dependence is due to the  $x$  dependence of the interatomic hopping matrix elements  $T_{\lambda\lambda'}$  and single-electron energies, which, in turn, is caused by the dependence of the lattice parameters on  $x$ . Thus, the single-electron mechanism also takes place in the usual tight-binding model. The many-electron mechanism arises in the GTB method as the effect of strong electron correlations.

### 3. LDA CALCULATIONS OF THE ELECTRONIC STRUCTURE OF $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ AND COMPUTATION OF THE MODEL PARAMETERS

$\text{Nd}_2\text{CuO}_4$  crystals have a tetragonal structure with space group  $14/mmm$  [4], which is also known as the  $T'$  structure (Fig. 1). The lattice parameter values are  $a = b = 3.94362 \text{ \AA}$  and  $c = 12.1584 \text{ \AA}$  [4].

The copper ions in the positions  $2a(0, 0, 0)$  are surrounded by four oxygen ions O1 located in the positions  $4c(0, 0.5, 0)$ . The Nd ions are in the positions  $4e(0, 0, 0.35112)$  and have eight nearest neighbor oxygen ions O2 in the positions  $4d(0, 0.5, 0.25)$  [4]. In contrast to the high-temperature tetragonal structure of  $\text{La}_2\text{CuO}_4$ , the  $T'$  structure of  $\text{Nd}_2\text{CuO}_4$  does not contain apex oxygen ions around the copper ions (Fig. 1). With cerium doping, the symmetry group of  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  is preserved, but the lattice parameters and the coordinate  $z$  of the neodymium ions are changed (Table 1) [4, 5].

The electronic structure of  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  is calculated for  $0 \leq x \leq 0.20$  within LDA. For this purpose, we employed the linearized muffin-tin orbital (LMTO)



**Fig. 1.** Crystal structure of  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ . The  $T'$  and  $T$  phases of the HTSC compounds  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  (to the left) and  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (to the right) are compared. Local distortions in the  $\text{CuO}_2$  plane are shown in the middle.

method within the tight-binding approximation using the atomic sphere approximation (TB-LMTO-ASA) [6, 7]. In the calculations, the Nd  $4f$  states are considered as quasi-core ones, because they are strongly localized and are much deeper than are the  $d$  states (see, e.g., [8]). The LDA-calculated band structure of  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  for high-symmetry directions in the Brillouin zone is shown in Fig. 2 by dashed lines. The set of bands formed by the hybrid Cu  $3d$  and O  $2p$  states is about 9 eV in width. The hybridization of the Cu  $d_{x^2-y^2}$  orbitals and the corresponding  $p_{x,y}$  orbitals of the in-plane oxygen ions (O1) brings about the formation in the  $\text{CuO}_2$  plane of a bonding band located at energies of  $-5$  to  $-6$  eV and an antibonding band crossing the Fermi level. This set of the hybrid orbitals

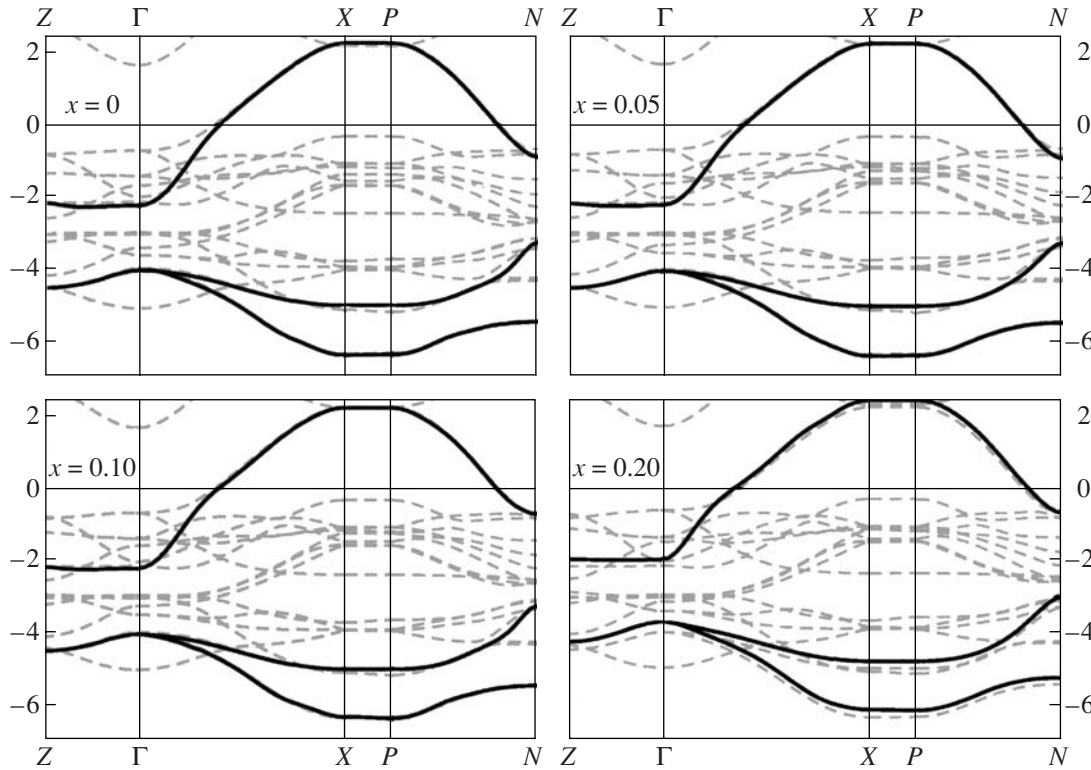
defines the noninteracting Hamiltonian of the so-called three-band  $p-d$  model.

The hopping integrals in the three-band  $p-d$  model are calculated using the NMTO ( $N$ th-order muffin-tin orbitals) method [9]. For the three hybrid bands of interest, we constructed the corresponding NMTO orbitals (solid lines in Fig. 2). It can be seen from Fig. 2 that the NMTO orbitals almost perfectly reproduce the bonding and antibonding bands of the hybridized  $d_{x^2-y^2}$  orbital of copper and  $p_{x,y}$  orbitals of oxygen obtained in complete LDA calculations. Thus, the low-dimensional Hamiltonian constructed in the basis of NMTO orbitals is the required Hamiltonian of the effective three-band model. Taking the Fourier transform of this effective Hamiltonian (defined in the  $\mathbf{k}$  space), we get the hopping integrals in the direct space as functions of the interatomic distance (Table 2). It is seen from Fig. 2 and Table 2 that the hopping integrals change only slightly with increasing cerium doping level. Therefore, we may assume that the single-electron contribution to the evolution of the electronic structure of  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  with increasing cerium concentration is insignificant.

**Table 1.** Structure parameters of  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  for various Ce ion concentrations  $x$  [4, 5] (all parameters are in angstroms)

	$x$				
	0	0.05	0.10	0.15	0.20
$a$	3.94362	3.94056	3.94071	3.94224	3.94295
$c$	12.1584	12.1130	12.0945	12.0603	12.030
$z(\text{Nd})$	0.35112	0.3519	0.3523	0.3527	0.3531

In the three-band  $p-d$  model, we also need to know the values of the Coulomb ( $U$ ) and exchange ( $J$ ) parameters for Cu ions. These parameters for copper in the  $\text{La}_2\text{CuO}_4$  compound were calculated in [10] using the supercell method [11]:  $U = 10$  eV and  $J = 1$  eV.



**Fig. 2.** Comparison of LDA-calculated electron dispersion curves (dashed lines) with dispersion curves for the effective noninteracting three-band Hamiltonian constructed in the basis of NMTO orbitals (solid lines) for various Ce concentrations  $x$ .

These values are used in the present paper for the  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  compound.

#### 4. LDA + GTB CALCULATIONS OF THE ELECTRONIC STRUCTURE WITH INCLUSION OF THE SINGLE-ELECTRON AND MANY-ELECTRON EFFECTS

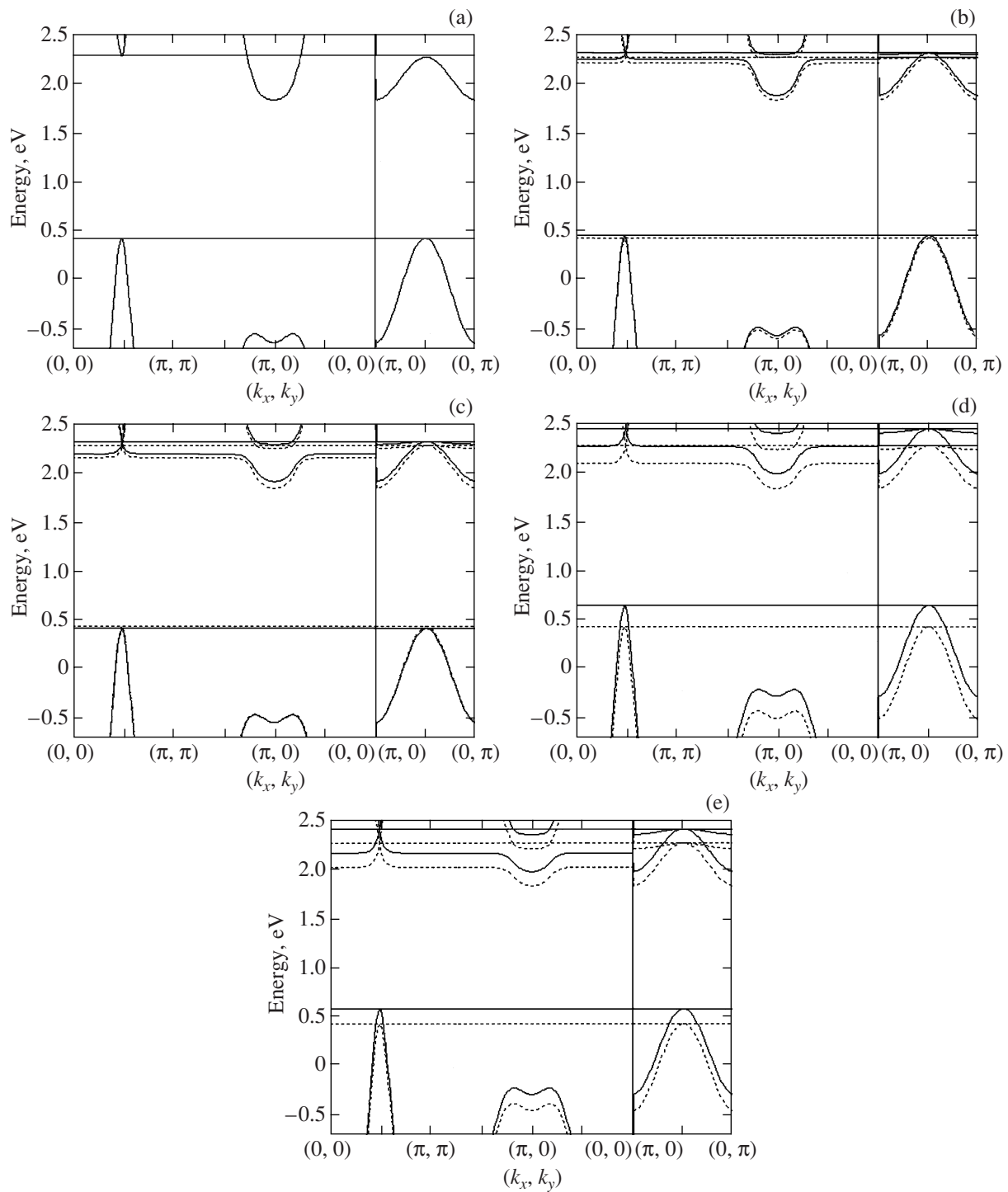
Over a wide range of dopant concentrations,  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  remains in the AFM phase. Therefore,

we first consider the changes in the band structure with doping in the AFM phase. Dispersion curves calculated from Eq. (1) for these doped compounds in the Néel state using the GTB + LDA method are shown in Figs. 3a–3e. Each panel shows the results of two calculations for the given carrier concentration: (i) using the parameter values obtained at  $x = 0$ , i.e., in the absence of the single-electron mechanism (Table 2), but taking into account the many-electron mechanism and (ii) using the real parameters of the Hamiltonian

**Table 2.** Hopping integrals and single-electron energies (in electronvolts) as functions of Ce ion concentration  $x$  for  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  obtained by the NMTO method ( $x^2$ ,  $p_x$ , and  $p_y$  denote the Cu  $d_{x^2-y^2}$  and O1  $p_{x,y}$  orbitals, respectively)

Hopping integral	Direction	$x$				
		0	0.05	0.10	0.15	0.20
$E(x^2 - y^2)$		-2.2855	-2.2847	-2.1760	-2.4215	-2.3507
$E(p_x)$		-3.2935	-3.3064	-3.2829	-3.2607	-3.2800
$t(x^2, p_x)$	(0.5, 0)	1.1216	1.1454	1.1665	1.1614	1.1726
$t'(x^2, p_x)$	(0.5, 1)	-0.0504	-0.0359	-0.0211	-0.0202	-0.0166
$t''(x^2, p_x)$	(1.5, 0)	0.0834	0.0921	0.1173	0.1130	0.1203
$t'''(x^2, p_x)$	(1.5, 1)	-0.0149	-0.0083	0.0015	0.0090	0.0153
$t(p_x, p_y)$	(0.5, 0.5)	0.8320	0.8389	0.8381	0.8365	0.8386
$t'(p_x, p_y)$	(1.5, 0.5)	0.0266	0.0331	0.0452	0.0450	0.0469





**Fig. 3.**  $\mathbf{k}$  dependences of the energies of quasiparticle states calculated using the LDA + GTB method for various concentrations  $x$ : (a) 0, (b) 0.05, (c) 0.10, (d) 0.15, and (e) 0.20. Dotted lines are calculations ignoring the single-electron mechanism of the concentration dependence, i.e., for the Hamiltonian parameters taken at  $x = 0$ . Solid lines are calculations taking into account both the many-electron and single-electron mechanisms.

depending on the dopant concentration (Table 2) with inclusion of the many-electron mechanism.

The calculated electronic structure of the undoped material ( $x = 0$ , Fig. 3a) reproduces the main effects of strong electron correlations in this compound. At the

bottom of the conduction band and at the top of the valence band, there are in-gap states, with their spectral weight being proportional to the doping level of the compound [12]. As the concentration of carriers  $x$  (electrons in our case) is increased, the in-gap

states at the conduction band bottom acquire dispersion and a nonzero spectral weight (Figs. 3b–3e). This is the main effect of the doping in the LDA + GTB method.

It can be seen in Fig. 3 that, for each concentration, the inclusion of the single-electron mechanism leads to almost uniform displacements of the top of the valence band and bottom of the conduction band. The displacement is negligible in the region of stability of the AFM state ( $x < 0.15$ ). As  $x$  increases further, the shift increases up to 0.15 eV at  $x = 0.2$ . However, this value is obtained by extrapolating the calculations to the region where the AFM phase no longer exists: hence, this value bears no relation to reality. As is seen from Figs. 3a–3e, the shifts of the in-gap states are about the same as those of the conduction band bottom (or the top of the valence band). Therefore, these shifts do not impede the formation of in-gap states near the bottom of the conduction band due to strong electron correlations.

Thus, it can be concluded that fine tuning of the parameters of the Hamiltonian depending on the dopant concentration causes the electronic structure in the vicinity of the insulating gap to shift as a whole, which is immaterial for the physics of HTSC.

## 5. CONCLUSIONS

In this paper, the influences of the single-electron and many-electron mechanisms of the concentration dependence of the electronic structure of the HTSC compound  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  have been studied jointly for the first time. The calculations of the electronic structure have been performed using the hybrid LDA + GTB method. It has been demonstrated that the strongest influence on the electronic structure is exerted by the many-electron mechanism and that the single-electron mechanism produces only small quantitative corrections and does not change the picture qualitatively.

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