Comparison of band structures of the compounds La_2CuO_4 and Nd_2CuO_4

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The band structure of the quasiparticles of the undoped dielectric compounds La_2CuO_4 and Nd_2CuO_4 is calculated with allowance for the strong electron correlations in the generalized tight-binding method. The dielectric gap in both compounds is determined mainly by charge-transport processes. The decrease of the gap on going from La to Nd is described by the decrease of the parameter $\delta = \varepsilon_p - \varepsilon_d$ (ε_p and ε_d are the energies of the single-particle states of the p- and d-holes), with the remaining parameters of the theory unchanged.

1. INTRODUCTION

The electron structure of the undoped compounds La_2CuO_4 and Nd_2CuO_4 is characterized by a dielectric gap E_g which is not accounted for by the standard band computations that yield a metallic state. The difficulties of the band theory are caused by strong electron correlations.

In simplified models of the electron spectrum with strong correlations, such as the Hubbard or Emery model, the dielectric gap for the case of one hole per A_2CuO_4 molecule A = La,Nd, corresponding undoped potentials, differs from zero. The gaps in the different models differ in nature. The most prevalent opinion is that the large Mott–Hubbard gap contains an occupied band of p-type oxygen states (valence band) separated from the empty upper Hubbard band (conduction band) by a gap with charge transfer.

No first-principles calculations with adequate allowance for strong correlations are available at present. There are two known approximate schemes that include strong correlations and lead to a dielectric gap (and to a magnetic moment $\approx 0.5\,\mu_B$ per Cu ion). The first is close enough to the traditional approximation and differs by the correlation of the potential when twofold occupied states are taken into account.[1] The gap is then of exchange origin and is produced between different spin subbands.

A fundamentally different scheme, which can be dubbed a generalized tight-binding method, was proposed by us in Refs. 2 and 3. Allowance for the strong correlations is made here directly following the construction of the multielectron orbitals. Hops between neighboring molecular orbitals are described in the spirit of a multilevel model of the Hubbard type. Calculation of the quasiparticle spectra in the "Hubbard-I" approximation leads to a dielectric band structure with a gap determined mainly by charge umklapp processes.

The aim of the present paper is to use the method of Refs. 2 and 3 to calculate and compare the band structures of La_2CuO_4 and Nd_2CuO_4. A brief description of the multielectron model and of the calculation method is given in Secs. 2 and 3. The calculation results are analyzed in Sec. 4.

2. MULTIELECTRON MODEL OF COPPER OXIDES

It follows from the aggregate of photoelectronic data that the bottom of the conduction band and the valence band are formed at a depth 6–7 eV by p-orbitals of oxygen and d-orbitals of copper. The remaining occupied states lie lower and the empty ones higher. We confine ourselves therefore to calculation of hybridized p–d states of the CuO_2 plane, assuming that the strong-correlation effects are immaterial for the remaining empty and filled bands, which can be obtained from the standard band computations and simply superimposed on the p–d bands of strongly correlated electrons.

We express the Hamiltonian of the p and d electrons of the CuO_2 plane in the hole representation;

$$\begin{aligned}
&H=H_d+H_p+H_{pd}+H_{pp},\\
&H_d=\sum_r H_d(r),\quad H_d(r)=\sum_{\lambda\sigma}\Big[(\varepsilon_{d\lambda}-\mu)\,d^{+}_{r\lambda\sigma}d_{r\lambda\sigma}\\
&\qquad+\frac{1}{2}U_d n_{r\lambda}{}^{\sigma}n_{r\lambda}{}^{-\sigma}\Big]+\sum_{\sigma\sigma'}(V_d n_{r1}{}^{\sigma}n_{r2}{}^{\sigma'}-J_d d^{+}_{r1\sigma}d_{r1\sigma'}d^{+}_{r2\sigma'}d_{r2\sigma}),\\
&H_p=\sum_i H_p(i),\quad H_p(i)=\sum_{\alpha\sigma}\Big[(\varepsilon_{p\alpha}-\mu)\,p^{+}_{i\alpha\sigma}p_{i\alpha\sigma}\\
&\qquad+\frac{1}{2}U_p n_{i\alpha}{}^{\sigma}n_{i\alpha}{}^{-\sigma}\Big]+\sum_{\sigma\sigma'}(V_p n_{i1}{}^{\sigma}n_{i2}{}^{\sigma'}-J_p p^{+}_{i1\sigma}p_{i1\sigma'}p^{+}_{i2\sigma'}p_{i2\sigma}),\\
&H_{pd}=\sum_{\langle i,r\rangle}H_{pd}(i,r),\\
&H_{pd}(i,r)=\sum_{\alpha\lambda\sigma\sigma'}(T_{\lambda\alpha}p^{+}_{i\alpha\sigma}d_{r\lambda\sigma}+\text{H.c.}+V_{\lambda\alpha}n_{r\lambda}{}^{\sigma}n_{i\alpha}{}^{\sigma'}\\
&\qquad-J_{\lambda\alpha}d^{+}_{r\lambda\sigma}d_{r\lambda\sigma'}p^{+}_{i\alpha\sigma'}p_{i\alpha\sigma}),\\
&H_{pp}=\sum_{\langle i,j\rangle}\sum_{\alpha\beta\sigma}(t_{\alpha\beta}p^{+}_{i\alpha\sigma}p_{j\beta\sigma}+\text{H.c.}),
\end{aligned}\tag{1}$$

where ε_p and ε_d are the single-particle energies of the p and d holes, U_p (U_d) and V_p (V_d) are the matrix elements of the intra-atomic Coulomb repulsion by one and by different orbitals of oxygen (copper), J_p and J_d are the Hund exchange integrals, $T_{\lambda\alpha}$ and $t_{\alpha\beta}$ are matrix elements of the p–d and p–p hops between nearest neighbors, and $V_{\lambda\alpha}$ and $J_{\lambda\alpha}$ are matrix elements of the Coulomb and exchange interactions of the nearest copper–oxygen neighbors.

The first two terms in (1) describe the intra-atomic en-

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ergies with allowance for the Hubbard correlations U_d and U_p, of the Coulomb interactions on various orbitals λ, and Hund exchange. The last two terms in (1) describe interatomic *p–d* hops and interactions and *p–p* hops. The essential orbitals are $d_{x^2-y^2}$ ($\lambda = 1$) and d_{z^2} ($\lambda = 2$), for copper and p_x ($\alpha = 1$) and p_y ($\alpha = 2$) for oxygen; we put

$$T_{x^2-y^2,\,p_x}=T_{pd},\quad V_{x^2-y^2,\,p_x}=V_{pd},\quad J_{x^2-y^2,\,p_x}=J_{pd},\quad t_{x,y}=t_{pp}.$$

3. TIGHT-BINDING METHOD WITH ALLOWANCE FOR ELECTRON CORRELATIONS

It is known that good account is taken of correlations in the atomic limits of Hubbard-type models, and of interatomic hops in the band limit. To take adequate account of the correlations and covalent effects, a cluster method of calculation was proposed in Refs. 2 and 3.

The gist of the method is the following: during the first stage the lattice is broken up into nonoverlapping cells (clusters), inside of which the Hamiltonian of the small cluster is diagonalized and Hubbard operators are constructed on the states of the cluster. During the second stage the interaction between the nearest states from different clusters can be exactly rewritten in terms of the interaction between the clusters. As a result, the Hamiltonian (1) takes the form of a generalized multilevel Hubbard model:

$$H=H_0+H_1,$$

$$H_0=\sum_{f\gamma n}(E_{n\gamma}-n\mu)X_f^{\gamma\gamma},$$

$$H_1=\sum_{\langle f,g\rangle}\sum_{\substack{\gamma\gamma' \\ \Gamma\Gamma'}}\Lambda_{\Gamma'\Gamma}^{\gamma\gamma'}(f,g)X_f^{\gamma\gamma'}X_g^{\Gamma'\Gamma}, \qquad (2)$$

where $\Lambda_{\Gamma\Gamma'}^{\gamma\gamma'}$ are the intercluster matrix elements, the sites f and g number the clusters, $E_{n\gamma}$ are the energy levels of the n-hole terms $|\gamma\rangle$ of the cluster, and $X_f^{\alpha\beta} = |\alpha\rangle\langle\beta|$. Whereas in the standard Hubbard model the cell (at the lattice point) contains four states, the number of states here is large and depends on the size of the cell and on the dimensionality of the basis of the *p*- and *d*-functions. Even in the simplest case considered in Ref. 3, with two *d*-states and two *p*-states and with a cluster in the form of a CuO_2 molecule, the number of the states in the cell is ~ 100. In a computer calculation, nevertheless, consideration of such a multilevel model is possible.

The spectrum of the single-particle hole excitations of the Hamiltonian H_0 consists of a set of nondispersive energy levels ("resonances") $\Omega_m = E_{n+1,\gamma_1} - E_{n,\gamma_2}$, where the subscript m numbers the Fermi excitations between the terms $|\gamma_2\rangle \to |\gamma_1\rangle$. The ground states of undoped La_2CuO_4 and Nd_2CuO_4 correspond each to one hole per cell ($n = 1$), and we designate the corresponding terms by $E_{1\gamma}$. The vacuum state p^6d^{10} corresponds to the term E_0. For $n = 1$ and $T = 0$, the only occupied resonance from among the entire aggregate of resonances $E_{1\gamma} - E_0$ is the lower Ω_0 corresponding to the ground term $n = 1$, while the remaining are empty. The levels $\Omega_m = E_{2\gamma_1} - E_{1\gamma_2}$ corresponding to excitation of two-hole states of a cluster are likewise not occupied.

Intercluster hops described by the Hamiltonian H_1 are taken into account by a perturbation theory, the simplest variant of which is known as the "Hubbard I" approximation. In this approximation the dispersion equation for the Brillouin zone corresponding to a two-sublattice structure is of the form

$$\det\{\delta_{mn}\delta_{AB}(\omega-\Omega_m)-F_m[A_{AB}{}^{mn}(k)+B_{AB}{}^{mn}(k)]\}=0. \qquad (3)$$

The subscripts A and B label here the sublattices, and the factor F_m depends on the occupation numbers, with $F_m = 1/2$ for $T = 0$ and $n = 1$; the matrices $A(k)$ and $B(k)$ correspond to the intercluster *p–p* and *p–d* hops and their explicit form is given in Ref. 3.

4. BAND STRUCTURES OF La_2CuO_4 and Nd_2CuO_4

Just as in the usual tight-binding method, the calculation results depend on the parameters of the model. There are at present no first-principles calculations of multielectron matrix elements. We have therefore determined the parameters by comparison with experiment. Preliminary results for La_2CuO_4 are given in Ref. 3, where photoelectron spectroscopy data were used together with the value of the magnetic moment per copper ion. The resultant parameters were not single-valued, and a rather wide range of parameters agreed with the results.[4] We use therefore additionally in the present paper a dielectric gap $E_g = 2.0$ eV for La_2CuO_4 and $E_g = 1.6$ eV for Nd_2CuO_4 (Ref. 5), so that the resultant parameters of the Hamiltonian are less multiple-valued.

Figure 1a shows the band structure of La_2CuO_4, calculated for the following values of the parameters (in eV):

$$\begin{gathered} U_d=U_p=\infty,\ V_d=4{,}5,\quad V_p=3,\ V_{pd}=0{,}6, \\ J_p=J_d=0{,}5,\ J_{pd}=0{,}2,\ T_{pd}=1, \\ t_{pp}=0{,}2,\ \delta=\varepsilon_{px}-\varepsilon_{d_{x^2-y^2}}=2, \\ \Delta_d=\varepsilon_{d_{z^2}}-\varepsilon_{d_{x^2-y^2}}=1{,}5,\ \Delta_p=\varepsilon_{py}-\varepsilon_{px}=0{,}8. \end{gathered} \qquad (4)$$

The energy origin is chosen to be a localized resonance level near the top of the valence band. It must be emphasized that the upper conduction band on the figure contains precisely one state per CuO_2 layer, notwithstanding the double degeneracy in spin. This is the result of including strong correlations in the zeroth-approximation Hamiltonian. Therefore in the hole representation for La_2CuO_4 the conduction band is fully occupied by one hole per CuO_2 layer, so that the Fermi layer lands inside the gap and the ground state is a dielectric. This constitutes the fundamental difference between our method and the usual band calculations.

The greater part of the bands are of the form of mixed *p–d* states, but with different fractions of the *p* and *d* states in the different bands. The top of the valence band is made up mainly of *p*-orbitals of oxygen with a small admixture ($\approx 10\%$) of $d_{x^2-y^2}$ states and an even smaller one ($\sim 1\%$) of d_{z^2} states of copper. The largest dispersion in the valence band is possessed by the *p*-band made up of oxygen–oxygen hops, with energy -1.2 eV at the point X and -0.2 eV at the point Γ. The figure shows not the entire valence *p–d* band, which is 6 eV wide, but only its upper half, which is the most important for the low-energy excitations.

The dielectric shell is more complicated than in the

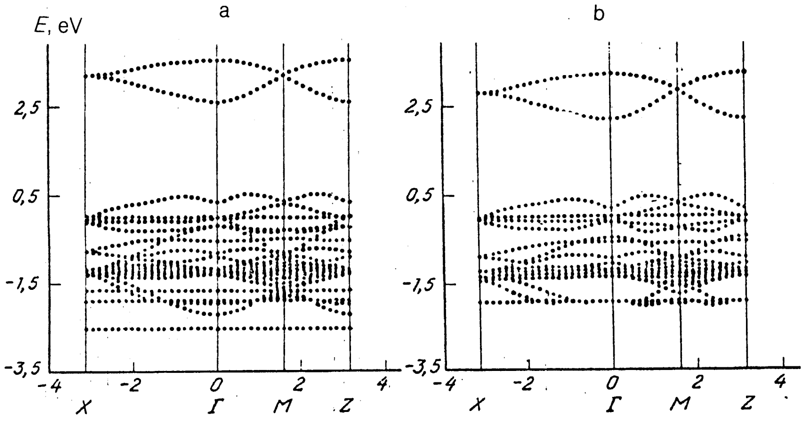

FIG. 1. Electron band structure of La_2CuO_4 (a) and Nd_2CuO_4 (b) (only the upper part of the valence band is shown).

classification of Ref. 6. It is determined by the charge-transfer energy and by the p–d hopping integral T_{pd}, as well as by the Coulomb matrix elements V_{pd} and J_{pd}. The main contribution is nonetheless determined by the gap with the charge transfer.

On going from La_2CuO_4 to Nd_2CuO_4 we assume that the greatest change occurs in charge-transfer energy δ. Since the Cu–O distance hardly changes, all the interatomic parameters are conserved. The crystal-field changes due to the absence of apical oxygen in Nd_2CuO_4 cause the levels ε_p and ε_d to shift so that it is just the parameter δ which is renormalized.

Figure 1 shows the Nd_2CuO_4 band structure obtained for $\delta = 1.4$ eV and the remaining parameters out of the set (4). The narrowing of the dielectric gap was accompanied also by other changes compared with La_2CuO_4. Thus, the p band due to the oxygen–oxygen jumps became narrower. A narrow gap appeared in the p–d valence band and led to a dip in the density of state in an energy region 1 eV lower than the top of the valence band. At the same time, the states near the bottom of the conduction band and the top of the valence band changed little. The former are determined as before mainly by the $d_{x^2-y^2}$ states of the copper, and the latter by the p_σ states of the oxygen.

The 0.6 eV change in the parameter δ on going from La_2CuO_4 to Nd_2CuO_4 is of the same order as the contribution of the apical oxygen, if the latter is estimated in the point-charge model.

5. CONCLUSION

The band structures of the undoped dielectrics La_2CuO_4 and Nd_2CuO_4 are thus qualitatively similar. The quantitative difference results mainly from the presence of apical oxygen in the former case and its absence in the latter.

With respect to the band structure of the doped $La_{2-x}Sr_xCuO_4$ and $Nd_{2-x}Ce_xCuO_4$, the situation is here more complicated. Preliminary results within the framework of our computation method show that the rigid-band model is not valid here. The Fermi level is not shifted into the interior of the valence band by hole doping or into the interior of the conduction band by electron doping. Instead, additional levels of the deep impurity-level type are produced at low impurity density, and the fraction of the d_{z^2} states of copper on these levels increases. The question, within the scope of the above approach, of formation of an impurity band, and of its intersection with the ground-state bands remains open at present.

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