

Variations in the density of states with doping of CuO₂ layers by holes

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(Submitted 21 October 1992)

Zh. Eksp. Teor. Fiz. **103**, 1404–1410 (April 1993)

The single-particle density of states is calculated for a CuO₄ cluster by direct diagonalization of the many-electron Hamiltonian. A dielectric gap exists in the undoped case, in which new states appear in connection with doping by holes. The concentration dependence of the Fermi level is found, and the critical concentration of the insulator–metal Anderson transition is estimated.

The conclusion concerning formation of new deep impurity states when La_{2-x}Sr_xCuO₄-type systems are doped by holes can be assumed to have been established quite reliably.¹ At the same time the details of their locations inside the insulating gap, as well as the location of the Fermi level, remain unclear and inconsistent (for example, the conclusions of Ref. 2 are in disagreement with those of Ref. 1).

Electron structure calculations of weakly doped copper oxides from first principles are impossible at the present time. The reason is the strong electron correlations, giving rise to the basic dielectric arrangement in the undoped case. Using a realistic many-electron model we have suggested a generalized tight-binding method,³ explicitly including strong electron correlations. In the first phase one carries out exact diagonalization of the CuO₂ cluster, and in the second—an approximate one, taking into account intercluster hoppings in the spirit of the “Hubbard I” approximation.

It seems that the pattern of the density of states $N(E)$ is basically determined by intracenter excitations, while intercenter hops only broaden the peaks of $N(E)$ with a typical band width ~ 0.5 eV. Therefore, for weakly doped oxides the main distinction from the undoped case is caused by the close neighborhood of the impurity center. The simplest model of an impurity center is a CuO₄ cluster with an excess hole in the cluster.

In the present study we report results of calculations of the density of states for a CuO₄ cluster, carried out by exact diagonalization of the many-electron Hamiltonian of the generalized Hubbard model. It seems that in a system with strong correlations there exists a specific formation mechanism of induced doping states inside the insulating gap.

The model consists of the minimum set of states which are important for the layer: these are the two $d_{x^2-y^2}$ - and d_{z^2} -orbitals of copper, and the two p_x - and p_y -orbitals of each oxygen ion. The explicit form of the Hamiltonian is given in Ref. 3, and contains the following terms: the single-hole energies of the 10 orbitals provided above with splitting parameters in the crystalline field $\Delta_d = \varepsilon_{z^2} - \varepsilon_{x^2-y^2}$, $\Delta_p = \varepsilon_y - \varepsilon_x$, the charge transport energy $\delta = \varepsilon_x - \varepsilon_{x^2-y^2}$, the three Coulomb matrix elements of the intra-ion interaction at each ion—the Hubbard energy U_d (U_p), the interorbital Coulomb parameter V_d (V_p) and the Hund exchange J_d (J_p), the Coulomb and exchange Cu–O interaction matrix elements: V_{pd} and J_{pd} , Cu–O hops T_{pd} for $d_{x^2-y^2}$ and $T_{pd}/\sqrt{3}$ for the d_{z^2} -orbital, as well as oxygen-oxygen hops t_{pp} .

The cluster in question is a fragment of the La₂CuO₄ cell, which of course, is electrically neutral. Since lanthanum is trivalent, the neutral cell corresponds to (CuO₄)⁶⁻ or Cu²⁺O₄²⁻ clusters. Assuming vacuum terms in the hole de-

scription of s^0d^{10} for copper and p^6 for oxygen, in the undoped case the number of holes per cluster $n = 1$ is obtained. Similarly, in the doped case the electrically neutral cell of La_{2-x}Sr_xCuO₄ corresponds to a number of holes per cluster $n = 1 + x$.

For numerical diagonalization of small clusters one usually utilizes various modifications of the Lanczos method; we have also employed another method, consisting essentially of the following: The number of holes in the cluster is a conserved quantity; therefore in the subspaces with various fixed number of holes $n = 0, 1, 2$ the Hamiltonian blocks are diagonalized numerically exactly, and the eigenenergies and eigenstates $|n, \gamma\rangle$ are found, where the index γ labels all cluster states with a given number of holes n . One then constructs the Hubbard operators $X^{ab} = |a\rangle\langle b|$ from the cluster states, and the single-particle Green’s function is calculated exactly in the Hubbard operator representation.

The energy of single-particle excitations in a strongly correlated system is determined by the “resonances” $\Omega(\gamma_1, \gamma_2) = E_{n+1}(\gamma_1) - E_n(\gamma_2)$; it is obtained automatically in the Hubbard operator representation. Rather than the pair of numbers specifying the initial and final states during single-particle excitation, it is convenient to introduce the vector⁴

$$\alpha \equiv (n + 1, \gamma_1; n, \gamma_2) \rightarrow X(\alpha) \equiv X^{n+1, \gamma_1; n, \gamma_2},$$

in which case the single-particle Fermi operator for hole annihilation at site i and in the orbitals $\lambda, \sigma = \pm 1/2$ is

$$a_{i\lambda\sigma} = \sum_{ab} \langle a | a_{i\lambda\sigma} | b \rangle X^{ab} = \sum_{\alpha} v_{i\lambda\sigma}(\alpha) X(\alpha), \quad (1)$$

where the matrix elements $v_{i\lambda\sigma}(\alpha)$ are calculated explicitly, as the cluster eigenstates are known. Since the Hamiltonian is decomposed into diagonal blocks in the Hubbard operator representation, the exact single-particle Green’s function equals

$$\langle \langle a_{i\lambda\sigma} | a_{j\lambda'\sigma'}^+ \rangle \rangle_E = \sum_{\alpha} v_{i\lambda\sigma}(\alpha) v_{j\lambda'\sigma'}^*(\alpha) F(\alpha) (E - \Omega_{\alpha})^{-1}, \quad (2)$$

where $F(\alpha) = \langle [X(\alpha), X^+(\alpha)]_+ \rangle$ is the so-called terminal factor in the terminology of Ref. 4, equal to the sum of the occupation numbers of the initial and final many-electron states associated with the single-particle “resonance” α . As a result we obtain for the single-particle density of states

$$N(E) = \sum_{i\lambda\sigma} |v_{i\lambda\sigma}(\alpha)|^2 F(\alpha) \delta(E - \Omega_{\alpha}). \quad (3)$$

Note that the method developed here makes it possible

to combine exact cluster calculations with approximate account of p - d and p - p hops between clusters, leading to the appearance of narrow bands $\Omega_\alpha(k)$ instead of the cluster energies Ω_α , similarly to the band-structure calculation of undoped La_2CuO_4 and Nd_2CuO_4 carried out in Ref. 5. For the purpose of the present study the broadening mechanism of levels Ω_α is unimportant, and the dispersion in k is replaced by simpler broadening, replacing each delta-function in (3) by a Lorentzian curve with halfwidth ε . Curve 1 of Fig. 1 shows the density of states of an undoped CuO_2 layer, calculated with the model parameters selected for La_2CuO_4 from Ref. 5 (in eV):

$$\begin{aligned} U_d = U_p = \infty; \quad V_d = 4,5; \quad V_p = 3; \\ V_{pd} = 0,6; \quad J_d = J_p = 0,5; \\ J_{pd} = 0,2; \quad T_{pd} = 1,5; \quad t_{pp} = 0,2; \\ \delta = 2; \quad \Delta_d = 1,5; \quad \Delta_p = 0,8. \end{aligned} \quad (4)$$

The energy is taken in the hole representation, so the valence band is located above the conduction band.

The nature of the dielectric gap has been discussed in detail in Ref. 5, and here it is only noted that, along with the major contribution due to charge transport processes, there also exists a Coulomb contribution. In the undoped case the Fermi level is located in the gap. This is most obvious in the hole representation, since the empty conduction band is positioned with account of the spin of a single hole per cell (and not two, as is the case for free electrons, in consequence of Hubbard subband splitting).

Two approaches are possible in calculating a doped system with hole concentration $n_h = 1 + x$. In the first the

model parameters are unchanged, with only the hole concentration changing. In analogy with the rigid band model, it is natural to call this approach the rigid crystal model. In this case the whole concentration dependence is contained in the terminal factors $F(\alpha)$. Even in this approach it is clear that doping causes new states to appear, since several "resonances" satisfy $F(\alpha) \propto x$ and contribute only when there is doping. The density of states in the solid-crystal model is shown in Fig. 1, where the new states are seen to occur approximately in the middle of the gap; their intensity increases with x . The impurity state is a mixture of the $d_{x^2-y^2}$ function with the b_1 molecular orbital of the oxygen ions.

The second method takes into account the change in the Hamiltonian parameters due to the impurities as well. This is naturally called the impurity method. The most evident changes are the decrease in the quantity δ on account of the difference in the La^{3+} and Sr^{2+} electrostatic potentials (in the point-charge model this causes a change of 0.5–1 eV), and the decrease in the p - d hop because the O^- radius is smaller than that of O^{2-} . Following Ref. 3, the magnetic moment μ of the copper ion is determined from the ratio T_{pd}/δ . Since for small x the quantity μ does not change, it is assumed that $T_{pd}(x)/\delta(x) = T_{pd}(0)/\delta(0)$. For simplicity the remaining parameters are assumed unchanged, and their values are selected from (4). For $x \ll 1$, when the impurity correlation can be neglected, within the simplest approximation in impurity fluctuations we have

$$N(E, x) = (1 - x)N(E, 0) + xN(E, 1). \quad (5)$$

Figure 2 shows the density of states in the impurity model with $T_{pd} = 0.9$ eV, $\delta = 1.2$ eV. It is seen that in this approach the number of impurity levels and the shape of the

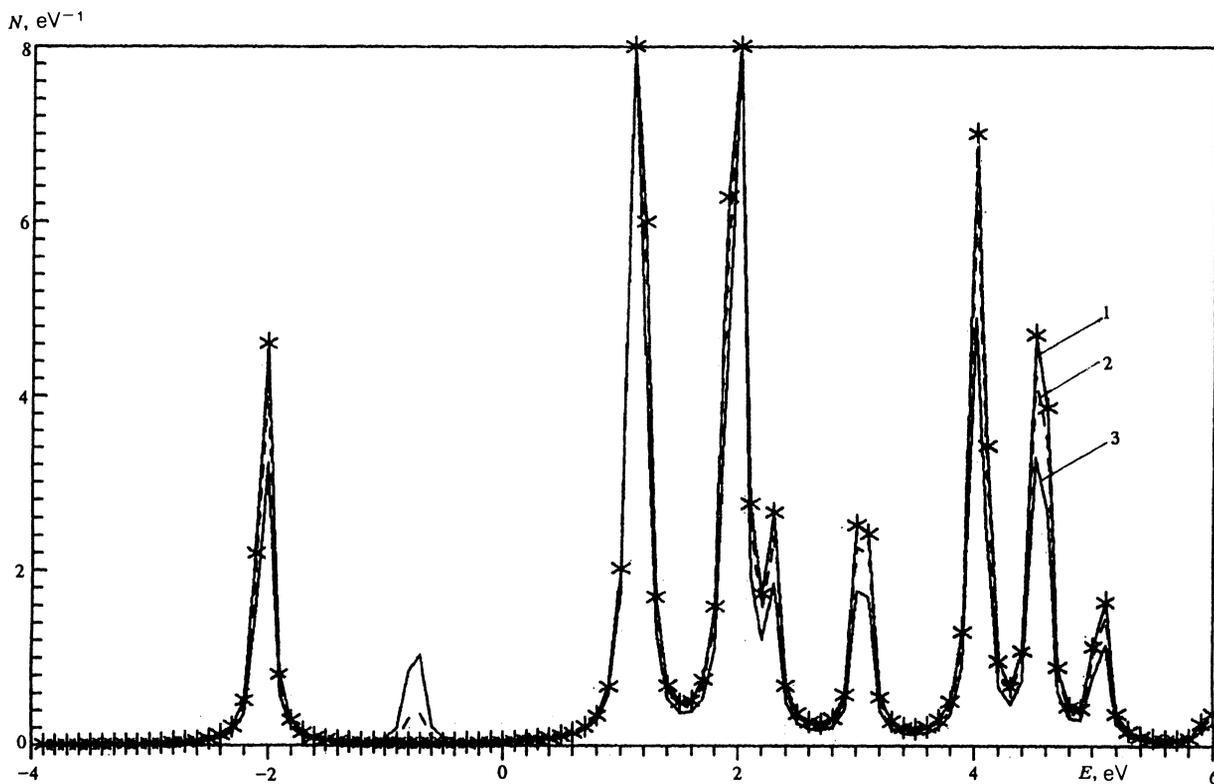


FIG. 1. The density of hole states in the rigid crystal model with the parameter of (4) and $\varepsilon = 0.05$ eV. Here: for 1) $x = 0$ —solid line with asterisks, 2) dots— $x = 0.1$, 3) solid line— $x = 0.3$.

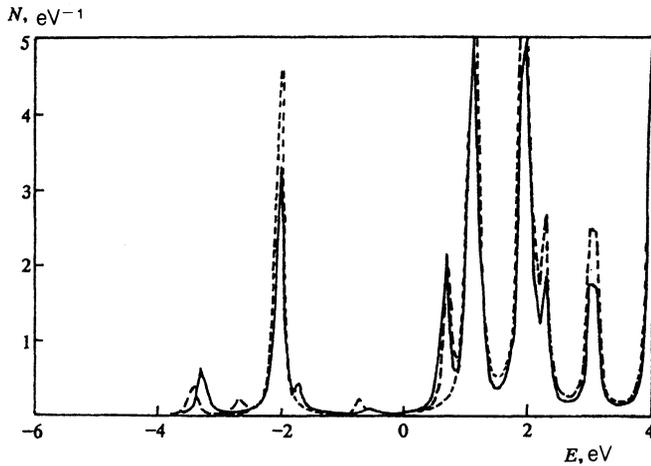


FIG. 2. The density of hole states in the impurity model with $T_{pd} = 0.9$ eV, $\delta = 1.2$, with the remaining parameters the same as in Fig. 1. Dots— $x = 0$, solid line— $x = 0.3$, dashed-dotted line— $x = 0.3$ for an orthorhombically distorted cluster.

$N(E)$ curve differ substantially from the rigid crystal model. The dashed curve in Fig. 2 shows $N(E)$ for a CuO_4 cluster with orthorhombic distortion, which was modeled by assigning various p - d hopping integrals along the x and y axes, $T_{pd}(x) = T_{pd} + a_1$, $T_{pd}(y) = T_{pd} - a_1$, $a_1 = 0.2$ eV. No significant differences were generated inside the gap. Figure 3 shows a high-resolution region inside the gap for two different concentrations, from which it is seen that for impurity levels $N(E) \propto x$.

Consider the nature of the states at the edge of the gap and inside it. As seen from Fig. 3, the top of the valence band consists of two peaks: for $E = 1.1$ eV it is a mixture of 35% d_{z^2} and 65% of a_1 oxygen molecular orbital (MO), and for $E = 1.2$ eV it is 13% of copper $d_{x^2-y^2}$ states, hybridized with 87% of b_1 oxygen MO. The closeness of these two bands was demonstrated earlier in Ref. 6. The bottom of the conduction band at $E = -2$ eV consists of $d_{x^2-y^2}$ states (almost 70%) and nearly 30% a_1 oxygen MO. Their hybridization partners, b_1 oxygen MO and d_{z^2} copper orbital, have an annihilation weight $\sim 1\%$. The impurity state with the largest spectral weight for $E_1 = 0.7$ eV is the $d_{x^2-y^2}$ mixture (12%) and the b_1 molecular orbital (88%) of oxygen. Two peaks with small spectral weights at $E_2 = -0.6$ eV and $E_3 = -1.7$ eV are formed mainly from the a_1 molecular orbital and the nonbinding orbital of oxygen.

The density dependence of the Fermi level is found by solving the equation

$$2 \int_{-\infty}^{\epsilon_F} N(E, x) dE = 1 + x. \quad (6)$$

Without doping the Fermi level is located near the middle of

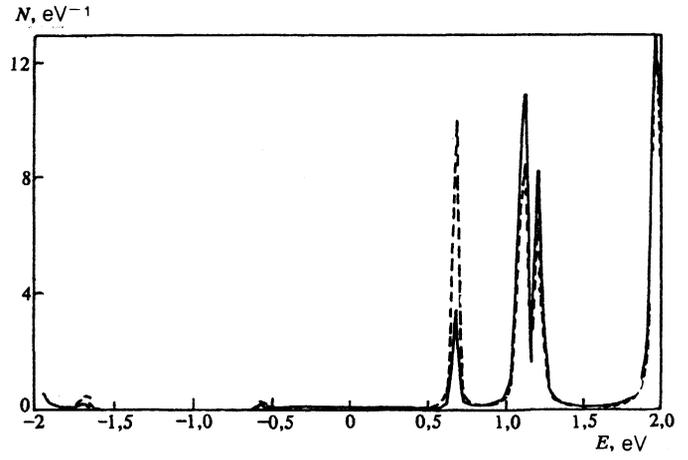


FIG. 3. The density of hole states inside the gap with improved resolution, $\epsilon = 0.01$ eV, with the same parameters as in Fig. 2. Solid line— $x = 0.1$, dots— $x = 0.3$.

the gap, $\epsilon_F = -0.75$ eV. For $x = 0.001$ the Fermi level is $\epsilon_F = -0.45$ eV and is near the E_2 impurity level. The number of states in this level is small, however. It fills up quickly and ϵ_F undergoes a further shift: for $x = 0.01$ we have $\epsilon_F = -0.2$ eV and for $x = 0.05$ we have $\epsilon_F = 0.5$ eV. We will estimate the critical concentration x_c of the insulator-metal Anderson transition, using the Mott criterion for the mobility threshold ϵ_c : $N(\epsilon_c) \approx 0.1 N_{\max}$.⁷ It is seen from Figs. 2 and 3 that $\epsilon_c = 0.6$ eV, with the ϵ_F value being reached at $x_c = 0.065$. This is in good agreement with the experimental value for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. With further increase in x the single-impurity approximation (5) is scarcely likely to hold, so Figs. 2 and 3 with $x = 0.1$ and $x = 0.3$ can be used only for illustration purposes, since at $x \sim 10^{-2}$ the impurity peaks are too low. For the mean distance between impurities near the insulator-metal transition point we obtain $l_c \approx 4a$.

If these results are extrapolated to the region $x \gtrsim x_c$, where the impurity peak E_1 spreads into a narrow band, the conclusion is reached that superconductivity is generated at concentrations such that ϵ_F is inside the narrow impurity pdG band, formed in the p_σ ground state of oxygen with symmetry b_1 .

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Translated by Nathan Jacobi