Electronic structure of the surfaces of layered copper oxides

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The electronic structure of the surfaces of layered copper oxides has been investigated in the framework of a tight-binding model together with the unrestricted Hartree-Fock method. The main element of the layered copper oxides, namely the CuO_2 layer, was supposed to lie parallel with the surface, as well as to be trimmed at a boundary of crystal. In the former case, the electrons at the surface were considered to be in an additional (surface) potential. A mode of the calculation of this potential has been developed on the basis of a method being similar to Ewald's transformation. As an example, the surface of La_2CuO_4 was studied. In the latter case, when the CuO_2 layer is semi-infinite due to its cutting at the surface, the formation of electronic surface bands was carefully investigated. Both the metal and dielectric phases were examined. For the metal phase, we took into account the possible freezing of the spin-density wave at the surface. In all the cases, surface bands were present in the vicinity of the Fermi level. They had inherent, in the one-dimensional systems, peculiarities.

I. INTRODUCTION

No great length of time has yet elapsed since the discovery of the high-temperature-superconducting property in layered copper oxides,[1] but its applications in different devices are already numerous and wide. Many of them are determined by or, at least, depend on properties of the surface, intergrain boundaries or interfaces. Theoretical investigations of the electronic structure of surfaces of layered copper oxides are yet few in number,[2] in spite of great attention to the problem from experimentalists (see, e.g., Refs. 3–8). This can be explained by the fact that the problem is too difficult and the objects are too complex. That is why, in this paper, we will try to find only qualitative approximation to the solution of the problem. For this purpose, we will use a simplest version of a tight-binding model in association with the unrestricted Hartree-Fock (UHF) method. This approach is appropriate for studying the ground dielectric state of undoped crystals as well as the metal state of doped crystals. That this approach holds for the qualitative description of the electronic structure of copper oxides, was carefully verified earlier in a few works.[9–11] It was shown that the values of the forbidden gap and the local magnetic moment, obtained within the UHF method, were in accordance with experiments for the dielectric phase. Moreover, the tight-binding method enables one to get a close approximation to the electronic band structure in the metal phase.[12–15] The $(pd\sigma)$ interactions between the neighboring oxygen and copper atoms in the single CuO_2 layer and the Hubbard interactions of electrons on the copper sites have only to be taken into account for this purpose.

The chemical bonds must be broken at the surface. As a result, a semi-infinite CuO_2 layer appears instead of the infinite one. In this paper, we will just investigate the electronic structure of the semi-infinite CuO_2 layer in the dielectric and metal phases. Due to drastic simplifications, results of the solution of the problem will be of common character and, consequently, be valid for the whole family of layered copper oxides. Some results will be obtained in an analytical form.

It is known that, in the case of point defects, the electron spectrum can conveniently be described by means of the Green function (GF) method. In this method, instead of the straightforward solution of the Schrödinger equation for the crystal as a whole, the problem of electron scattering at a potential point disturbance is addressed. In the case where the GF's of an ideal crystal are known, this problem is reduced to the solution of a usually small system of linear equations.

When dealing with surfaces, the GF method should be applied together with the method of the inverse Fourier transformation. This approach has been already actively implemented in the analysis of the electronic structure of surfaces in semiconductors.[16]

The plan of our paper is as follows. Section II is devoted to the description of the GF method. Section III deals with the electronic structure of the semi-infinite CuO_2 layer in the metal phase. In Sec. IV we take into account the possible antiferromangetic ordering at the surface. Section V considers the semi-infinite CuO_2 layer in the dielectric phase. The method of the calculation of the potential at the surface is presented in Sec. VI. Finally, Sec. VII draws the conclusions which we have obtained.

II. THE GF METHOD

Let us break the crystal up into slabs being parallel with the surface. We will use the representation $|n\mathbf{k}ij\alpha\rangle$, where n is the number of the slab, $\mathbf{k}$ is the wave vector lying in the plane of the slab, i is the number of an atom in the cell, j is the number of an orbital on the atom, and α is the spin projection. The Dyson equation written in this representation has a particularly simple form if the perturbation of the potential is uniform along the slab

$$\hat{G} = \hat{g} + \hat{g}\hat{V}\hat{G} , \qquad (1)$$

where $\hat{g}$ and $\hat{G}$ are the GF of the ideal and perturbed crystals, respectively. $\hat{V}$ is a matrix of the perturbation potential. Since the perturbation of the potential takes place in a restricted volume of the crystal, it is not too difficult to obtain the solution to Eq. (1) for sites possessed by this volume. Indeed, Eq. (1) in this case can be reduced to the ordinary system of linear inhomogeneous equations

$$(\hat{1}-\hat{g}\hat{V})\hat{G}=\hat{g} \ . \tag{2}$$

Having found this solution, we can then obtain the GF in bulk by making use of Eq. (1). The partial density of states is next determined by

$$N_L(\varepsilon)=-\frac{1}{\pi\Omega}\,\text{Im}\int_{BZ}G_{LL}(\varepsilon,k)d^2k \ , \tag{3}$$

where Ω is the area of the cell in the reciprocal space, $L\equiv(nij\alpha)$ is the set of the quantum numbers described above. The energy dispersion in surface bands can be obtained from the equation

$$D(\varepsilon,k)=\det\|\hat{1}-\hat{g}\hat{V}\|=0 \ . \tag{4}$$

To determine the density of states in these bands, let us employ the following maneuver. Let us shift the energy ε into the complex plane $\varepsilon\rightarrow\varepsilon+i\times0$ and write a formal solution to Eq. (2) with the help of Kramer's rule

$$G_{LL}=\frac{D_{LL}}{D} \ , \tag{5}$$

where D_{LL} is determinant (4) in which the column, corresponding to the state $|L\rangle$, is replaced by the column of free terms. Expanding the determinant $D(\varepsilon,k)$ in the vicinity of a solution of Eq. (4) $\varepsilon_1=\varepsilon_1(k)$ into a Taylor series, we have

$$D(\varepsilon,\mathbf{k})=D(\varepsilon_1,\mathbf{k})+D'_\varepsilon(\varepsilon_1)(\varepsilon-\varepsilon_1+i\times0)+\cdots \ . \tag{6}$$

Here $D'_\varepsilon(\varepsilon_1)$ is the partial derivative of $D(\varepsilon,\mathbf{k})$ with respect to ε at $\varepsilon=\varepsilon_1$. Note that, according to condition (4), the first term vanishes.

By substituting (6) into (5) and, thereafter, the GF obtained into (3), we find

$$N_L^1(\varepsilon)=\frac{1}{\Omega}\int_{BZ}\frac{D_{LL}}{D'_\varepsilon(\varepsilon_1)}\delta(\varepsilon-\varepsilon_1)d^2k \ . \tag{7}$$

Charges on atoms can be obtained by performing the integration over the occupied sites

$$q_L=\int_{\substack{\text{bulk}\\\text{bands}}}^{\varepsilon_F}N_L(\varepsilon)d\varepsilon+\int_{\substack{\text{surface}\\\text{bands}}}^{\varepsilon_F}N_L^1(\varepsilon)d\varepsilon \ . \tag{8}$$

The densities of states in the bulk and surface bands are given by Eqs. (3) and (7).

III. THE ELECTRONIC STRUCTURE OF THE SEMI-INFINITE CuO₂ LAYER IN THE METAL PHASE

A. The electronic structure of the ideal layer

The unit cell of the ideal CuO_2 layer is comprised of the copper (1) and two oxygen (2 and 3) atoms. We in-

clude into the basis of the tight-binding method only the $p\sigma$ state on the oxygen atoms and the $d_{x^2-y^2}$ state on the copper ones. We take into account interactions only between the nearest neighbors. In this simple case, the energy of electrons has the well-known form

$$\varepsilon_k^\nu=\varepsilon_0+\nu[\Delta^2+2t^2(2-C_x-C_y)]^{1/2} \ , \tag{9}$$

where ε_0, Δ are the half sum and half difference of the one-electron energies ε_p and ε_d, respectively, $\nu=\pm1$, t is the hopping integral for which we will use the value of $3^{1/2}V_{pd\sigma}/2$ where $V_{pd\sigma}=-1.85$ eV,[15] $C_\alpha=\cos k_\alpha a$, a is the lattice parameter. The vectors of the bonding and antibonding states can be expressed in the framework of this model as follows:

$$C_1^\pm=\left[\frac{\varepsilon^\pm-\varepsilon_p}{2(\varepsilon^\pm-\varepsilon_0)}\right]^{1/2} \ ,$$

$$C_2^\pm=t\frac{1-\exp(ik_ya)}{\sqrt{2(\varepsilon^\pm-\varepsilon_0)(\varepsilon^\pm-\varepsilon_p)}} \ , \tag{10}$$

$$C_3^\pm=t\frac{1-\exp(ik_xa)}{\sqrt{2(\varepsilon^\pm-\varepsilon_0)(\varepsilon^\pm-\varepsilon_p)}} \ .$$

The vectors of the nonbonding states vanish on the copper atoms and are given by the following expressions on the oxygen atoms:

$$C_2^0=-\exp\left[\frac{ik_ya}{2}\right]\left[\frac{1-C_x}{2-C_x-C_y}\right]^{1/2} \ ,$$

$$C_3^0=\exp\left[\frac{ik_xa}{2}\right]\left[\frac{1-C_y}{2-C_x-C_y}\right]^{1/2} \ . \tag{11}$$

Spectrum (9), in combination with vectors (10) and (11), gives a comprehensive description of the electronic structure of the ideal CuO_2 layer and, consequently, can be used as the basis for calculating the GF.

B. The GF of the ideal layer

As the Brillouin zone of the CuO_2 layer is represented by a square, the Fourier transforms of the GF can be determined by the following obvious formula:

$$g_{LM}(k_x)=\frac{a}{2\pi}\sum_\tau\int_{-\pi/a}^{\pi/a}\frac{C_L^{\tau*}C_M^\tau}{\varepsilon-\varepsilon_k^\tau+i\times0}dk_y \ , \tag{12}$$

where the summation is performed over the bands of the bonding, nonbonding, and antibonding states. Due to specialities of Eq. (9), the calculation of the GF can be reduced to the calculation of a universal function

$$g_1=\frac{\varepsilon-\varepsilon_p}{t}f(\xi_x) \ ,$$

$$g_2=\frac{\varepsilon-\varepsilon_d}{2t^2}f(\xi_x)+\left[\frac{1-C_x}{3-C_x}\right]^{1/2}\frac{1}{\varepsilon-\varepsilon_p+i\times0} \ ,$$

$$g_3=\frac{\varepsilon-\varepsilon_d}{2t^2}f(\xi_x)+\left\{1-\left[\frac{1-C_x}{3-C_x}\right]^{1/2}\right\}\frac{1}{\varepsilon-\varepsilon_p+i\times0} \ ,$$

$$g_{n1,02}=\frac{\varepsilon-\varepsilon_p}{t(\varepsilon-\varepsilon_0)}f(\xi_x)[1-z(\xi_x)]z(\xi_x)^n \ , \tag{13}$$

where

$$\xi_x = \frac{1}{2}(e - 4 + 2C_x) + i \times \text{sign}(\varepsilon - \varepsilon_0) \times 0 \ ,$$

$$e = \frac{(\varepsilon - \varepsilon_0)^2 - \Delta^2}{t^2} \qquad (14)$$

$$z(\xi) = \begin{cases} -\xi + \text{sign}(\xi)\sqrt{\xi^2 - 1} \ , & |\xi| > 1 \\ -\xi + i \times \text{sign}(\varepsilon - \varepsilon_0)\sqrt{1 - \xi^2} \ , & |\xi| < 1 \ . \end{cases} \qquad (15)$$

Here g_1 is the diagonal element of the GF for the column of the copper atoms, while g_2 and g_3 are the elements for the columns of the oxygen atoms. $g_{n1,02}$ is the nondiagonal element of the GF between the columns of the copper and oxygen atoms lying in the nth and 0th slabs, respectively, $f(\xi)$ is the universal function for which we have obtained the following analytical expression:

$$f(\xi) = \begin{cases} \dfrac{\text{sign}(\xi)}{2\sqrt{\xi^2 - 1}} \ , & |\xi| > 1 \\ \dfrac{-i \times \text{sign}(\varepsilon - \varepsilon_0)}{2\sqrt{1 - \xi^2}} \ , & |\xi| < 1 \ . \end{cases} \qquad (16)$$

C. The GF of the semi-infinite layer

To break chemical bonds up at the surface, one may eliminate the states of the nearest to the surface sites from the basis (Fig. 1). Indeed, the elimination of the chain made of the oxygen atoms (shown in Fig. 1) leads to the disruption of the layer into two separate parts because of taking into account only the nearest-neighbor interactions.

A mode of eliminating orbitals from the basis was earlier proposed by Bernholc and Pantelides.[17] For this purpose, it was suggested to direct the matrix element of the potential on the atom removed to infinity. Of course, it is not to be supposed that the potential at this site is infinite in reality. The same result could be achieved by vanishing of corresponding hopping integrals.

All said above makes it possible to obtain the GF of the semi-infinite layer. In pursuing this aim, one can use the following equations:

$$G_1 = g_1 + g_{01,02} V_{02} G_{02,01} \ ,$$

$$(17)$$

$$G_{02,01} = g_{02,01} + g_2 V_{02} G_{02,01} \ ,$$

where V_{02} is the potential on the removed oxygen atoms. The solution to Eqs. (17), after letting $V_{02} \to \infty$, takes the

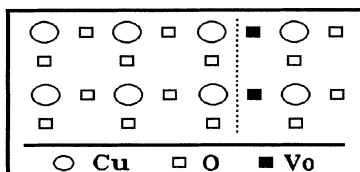following simple form:

$$G_1 = g_1 - \frac{g_{01,02}^2}{g_2} \ . \qquad (18)$$

The dependence of the GF on the column number can be then determined from the expression

$$G_{n1} = g_1 - \frac{g_{n1,02}^2}{g_2} \ . \qquad (19)$$

Now, the density of states on the copper atom in the nth slab may be represented as

$$N_{n1} = -\frac{a}{2\pi^2} \text{Im} \int_{-\pi/a}^{\pi/a} dk_x \left[g_1 - \frac{g_{n1,02}^2}{g_2} \right] \ . \qquad (20)$$

Specific results of calculating the GF and density of states for the CuO_2 layer will be given in the next sections.

D. Results of density-of-states calculations

Let us start with the calculation of the partial density of states on the copper atom of the ideal layer. By using Eq. (3) together with Eq. (13), we readily obtain

$$N_1^0(\varepsilon) = \frac{|\varepsilon - \varepsilon_p|}{2\pi^2 t^2} \theta[e(8 - e)] K \left[\frac{\sqrt{e(8 - e)}}{4} \right] \ , \qquad (21)$$

where $\theta(x)$ and $K(k)$ are the step function and the complete elliptic integral of the first kind, respectively. The density of states (21) is normalized to 1. This density has Van Hoves singularities and jumps typical of two-dimensional systems. In the metal- (doped) layer, the Fermi level lies somewhat below the logarithmic singularity located at $e = 4$.

Breaking the chemical bonds at the surface, we have the following change of the density of states on the copper atoms:

$$\Delta N_{n1} = \frac{a}{2\pi^2} \text{Im} \int_{|\xi_x| < 1} dk_x \frac{g_{n1,02}^2}{g_2} \ . \qquad (22)$$

Results of calculating this change vs n and ε are represented in Fig. 2. From this figure we notice that the electronic charge on the surface copper atom is greater than in bulk. We call attention to the fact that the number of oscillations in the change of the density of states
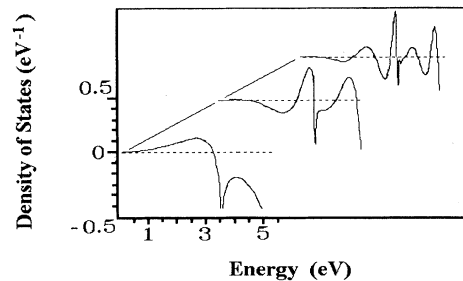

FIG. 1. The semi-infinite CuO_2 layer.

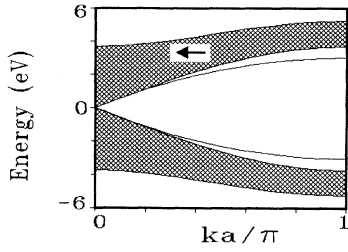FIG. 2. The change of the density of states on the copper atom (the CuO_2 layer in the metal phase).

FIG. 3. The energy dispersion in surface bands of the semi-infinite CuO_2 layer in the metal phase. The dashed area corresponds to the bulk's band.

increases with the distance from the surface. As a consequence, charges on atoms and other integral characteristics coincide with corresponding values for bulk not so far from the surface. However, differential characteristics sharply depend on the energy even very far from the surface.

E. Surface states

Condition (4) of surface states appearing in the electronic spectrum has in the considered case a particularly simple form

$$g_2(k_x, \varepsilon) = 0 \ . \tag{23}$$

Figure 3 represents the solutions to this equation in the range $\xi_x < -1$. One can see that the surface band overlaps the bulk's band. Its top lies somewhat below the energy of the Van Hove singularity in the density of states of the bulk. Thus, if the Fermi energy is shifted to the surface states by means of an acceptor's substitutions, surface conductivity and related phenomena would arise.

The partial density of states in the surface band can be expressed as follows:

$$N_{n1}^{surf}(\varepsilon) = -\frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} \frac{g_{n1,02}^2(\varepsilon_1)}{(\partial/\partial\varepsilon)g_2|_{\varepsilon=\varepsilon_1}} \delta[\varepsilon - \varepsilon_1(k_2)] dk_x \ , \tag{24}$$

where $\varepsilon_1 = \varepsilon_1(k_x)$ is a solution to Eq. (4). We have calculated this density and found it to have Van Hove singularities typical of one-dimensional systems and to be sharply decreasing with the distance from the surface (Fig. 4).
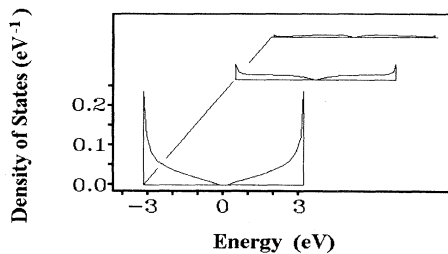

FIG. 4. The partial density of states on the copper atom in the surface band of the semi-infinite CuO_2 layer (the metal phase).

IV. THE ELECTRONIC STRUCTURE OF THE METALLIC CuO_2 LAYER TAKING INTO ACCOUNT THE POSSIBILITY OF THE ANTIFERROMAGNETIC ORDERING OF ELECTRONS ON THE SURFACE

A. The electronic structure of the ideal CuO_2 layer with a doubled cell

Breaking of chemical bonds at the surface leads to a lowering of the degree of covalency for the topmost atoms. In general, this can initiate a localization of electrons and, in particular, their antiferromagnetic ordering at the surface. The following is a consideration just of this case.

To describe the antiferromagnetic ordering, we double the unit cell of the infinite CuO_2 layer as shown in Fig. 5. The electron energy in the bands of the bonding and antibonding states has, in this case, the form

$$\varepsilon_k^{\mu v} + v\{\Delta^2 + 2t^2(2 - \cos k_y a)$$
$$+ \lambda t^2[2(1 - \cos 2k_x a)]^{1/2}\}^{1/2} \ , \tag{25}$$

where $v = \pm 1$, $\lambda = \pm 1$. The vectors of states needed for the calculations are described by the following expressions:

$$C_2 = \frac{1 - \exp(-ik_y a)}{\varepsilon - \varepsilon_p} C_1 \ , \quad C_4 = \frac{1 - \exp(-ik_y a)}{\varepsilon - \varepsilon_p} C_3 \ ,$$

$$|C_1| = |C_3| = \left[\frac{\varepsilon - \varepsilon_p}{4(\varepsilon - \varepsilon_0)}\right]^{1/2} \ . \tag{26}$$

This knowledge is sufficient for calculating the GF.

B. The GF of the ideal layer

Necessary computations can again be performed analytically that markedly facilitate the problem. The final results are

$$g_{n1,01} = \frac{\varepsilon - \varepsilon_p}{2t^2} \sum_\lambda z(\xi_\lambda)^n f(\xi_\lambda) \ ,$$

$$g_{n1,02} = \frac{1}{4t} \sum_\lambda [1 - z(\xi_\lambda)] z(\xi_\lambda)^n f(\xi_\lambda) \ ,$$

$$g_2 = \frac{\varepsilon - \varepsilon_d}{4t^2} \sum_\lambda f(\xi_\lambda) \tag{27}$$

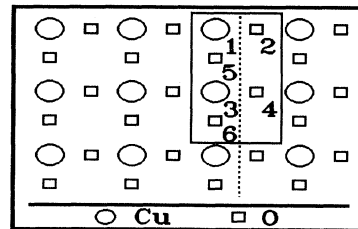$$+ \frac{1}{\varepsilon - \varepsilon_p + i \times 0} \left[\frac{1 - \cos(2k_x a)}{3 - \cos(2k_x a)}\right]^{1/2} \ ,$$

FIG. 5. The ideal CuO_2 layer with a doubled cell.

where

$$\xi_\lambda = \frac{1}{2}[e-4-\lambda\sqrt{2(1-\cos 2k_x a)}]$$
$$+ i \times \mathrm{sign}(\varepsilon - \varepsilon_0) \times 0 \ . \tag{28}$$

C. Results of calculations

We assume the perturbation potential on the topmost Cu column to be alternating between two values δ and $-\delta$

$$V_{01\alpha} = -\delta, \ \ V_{01\beta} = \delta, \ \ V_{03\alpha} = \delta, \ \ V_{03\beta} = -\delta \ . \tag{29}$$

The potentials on the surface oxygen atoms 2 and 4 are supposed to be infinite. Thus, the matrix of the perturbation potential describes in this case the change of the potential due to the antiferromagnetic ordering on the topmost copper column, as well as the breaking of chemical bonds between the surface copper and nearest oxygen atoms.

The value of the parameter δ depends, in general, on the Fermi-energy position and surface electrostatic potential. The study of these dependencies represents a special problem which is not of interest here. We want only to illustrate results of an ordering combined with the breaking of chemical bonds. For this purpose, we will make use of the value $\delta = 2$ eV obtained in self-consistent calculations carried out for the ideal dielectric CuO_2 layer.[10]

On the basis of the calculations performed, we have obtained that, as in the case of the metal layer, the electronic charge on the surface copper atoms increases, but this growth for the state with the spin projection $1/2$ differs from that found for the state with the spin projection $-1/2$. Thus, the increase in the charge on the surface copper atoms is accompanied by the ordering of the spin density. The number of oscillations within the definite energy interval increases with the distance of the column from the topmost one, and, as a result, the change of the charge on the copper atom rapidly vanishes with the distance.

Figure 6 represents the energy dispersion in the surface bands obtained from the condition of vanishing of the determinant D

$$(1-g_{01}V_{01\alpha})g_{02}+g_{01,02}^2 V_{01\alpha}=0 \ , \tag{30}$$

$$(1-g_{01}V_{01\beta})g_{02}+g_{01,02}^2 V_{01\beta}=0 \ . \tag{31}$$
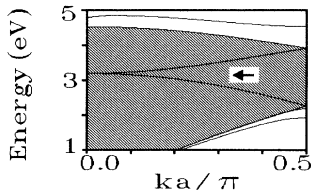
FIG. 6. The energy dispersion in surface bands of the metallic semi-infinite CuO_2 layer. The possible antiferromagnetic ordering on the surface is taken into account. The dashed area corresponds to the bulk's band.

The lower degenerate branches in Fig. 6 are solutions of Eq. (30). The basic functions $|01\alpha\rangle$ and $|03\beta\rangle$ dominate in these states. The upper branches correspond to the solution of Eq. (31). These states are made predominantly of $|01\beta\rangle$ and $|03\alpha\rangle$ orbitals.

Thus, the antiferromagnetic ordering on the surface leads to the splitting of the surface band (see Fig. 6). The first new branch lies above the bulk's band, while the second one lies under this band. There is a gap between these two branches of about 2 eV. The surface conductivity cannot in this case be a consequence of doping due to large splitting of the surface band.

We have studied the change of the total charge on the copper atom vs the distance from the surface and obtained it to be already saturated on the third column. However, it does not mean that the change of the spin density already vanishes there. The point is that the antiferromagnetic ordering of electrons on the first column initiates the same, but shifted, ordering in the next column and so on. In principle, the depth of such ordering should be determined by a self-consistent method but this laborious work is beyond the scope of the present article.

V. AN INVESTIGATION OF SURFACE STATES IN THE DIELECTRIC CuO_2 LAYER

A. The electronic structure of the ideal dielectric layer

Figure 7 depicts the unit cell of the antiferromagnetic CuO_2 layer. The copper atoms 1 and 3, as well as 2 and 4, are equal. The least-squares fitting of the results of band-structure calculations by the tight-binding method has shown that the Hartree-Fock energies of the $d_{x^2-y^2}$ level on the copper atom and the p_σ level on the oxygen atom are close to each other

$$\varepsilon_p = \varepsilon_d + n_d U \equiv \varepsilon_d^{HF} \ , \tag{32}$$

where n_d is the occupation number of the copper's $d_{x^2-y^2}$ level. The value of ε_p, at $U=7$ eV and $n_d=1/2$, is 3.5 eV above ε_d.[12-15]

Under condition (32), the electronic spectrum can be described analytically[18]

$$\varepsilon_k^{\nu\mu\lambda}=\nu\left\{\frac{2w+\delta^2}{2}+\mu\left[\frac{\delta^4}{4}+w\delta^2+v^\lambda\right]^{1/2}\right\}^{1/2} \ , \tag{33}$$
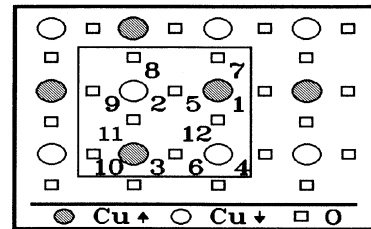
where $\nu=\pm 1$, $\mu=\pm 1$, and $\lambda=\pm 1$,

FIG. 7. The unit cell of the antiferromagnetic CuO_2 layer.

$$w = 4t^2 \ , \quad \delta = \frac{1}{2} U(n_{d\alpha} - n_{d\beta}) \ . \tag{34}$$

Here $n_{d\alpha}$ and $n_{d\beta}$ are the occupation numbers of the $d_{x^2-y^2}$ states with the spin projections α and β, respectively,

$$v^\lambda = 4t^4(\cos k_x a + \lambda \cos k_y a)^2 \ . \tag{35}$$

Spectrum (33) possesses two gaps, widths of which are equal and coincide with the value of the parameter δ. The upper and lower bands have, predominantly, the character of d states of Cu, while the central bands are mainly made of the $2p$ states of the oxygen atoms. This picture is consistent with spectroscopic experiments.[19]

B. The GF of the ideal layer

A general method of reducing the GF in the antiferromagnetic alternate lattice to universal functions was developed in Ref. 18. In the present case, the result is

$$g_1 = g_3 = -\frac{\varepsilon}{w^2}(w - \varepsilon^2 + \varepsilon\delta)f(e) \ ,$$

$$g_2 = g_4 = -\frac{\varepsilon}{w^2}(w - \varepsilon^2 - \varepsilon\delta)f(e) \ ,$$

$$g_5 = g_6 = -\frac{\varepsilon}{2w^2}(w + \delta^2 - \varepsilon^2)f(e)$$
$$+ \frac{1}{\varepsilon + i \times 0}\left[\frac{1-\cos(2k_x a)}{3-\cos(2k_x a)}\right]^{1/2} , \tag{36}$$

where

$$f(e) = \frac{a}{2\pi}\sum_\lambda \int_{-\pi/a}^{\pi/a} \frac{dk_y}{e - v^\lambda/w^2 + i \times \text{sign}(\mu) \times 0} \ ,$$

$$e = 1 + \frac{\varepsilon^2}{w^2}(\varepsilon^2 - 2w - \delta^2) \ , \tag{37}$$

$$\mu = \frac{2\varepsilon}{w^2}(2\varepsilon^2 - 2w - \delta^2) \ .$$

The following analytical expression was obtained for the universal function:[2]

$$f = -\frac{2^{3/2}(h+c)}{hc(hc+b)^{1/2}} \ , \tag{38}$$

where

$$h^2 = 4|e| + (1+C_x)^2 \ , \quad b = 4|e| - (1-C_x^2) \ ,$$
$$c^2 = 4|e| + (1-C_x)^2 \ .$$

Nondiagonal elements of the GF can be found from the approximate relations

$$g_{02,05} = \frac{t}{\varepsilon}g_2 \ , \quad g_{05,01} = \frac{t}{\varepsilon}g_1 \ ,$$
$$g_{03,06} = \frac{t}{\varepsilon}g_3 \ , \quad g_{06,04} = \frac{t}{\varepsilon}g_4 \ . \tag{39}$$

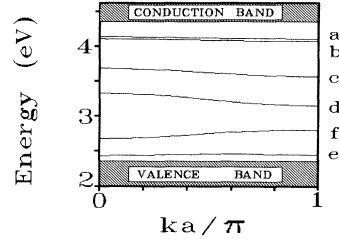We checked these connections numerically and found them to have reasonable precision. We took into account

FIG. 8. The energy dispersion of surface bands in the antiferromagnetic CuO$_2$ layer. The (100) edge formed by Cu atoms with (a) $s_z = 1/2$, $V_M = -1$ eV, (b) $s_z = 1/2$, $V_m = -2$ eV, (c) $s_z = -1/2$, $V_M = -1$ eV, (d) $s_z = -1/2$, $V_M = -2$ eV. The (100) edge formed by O atoms with (e) $V_p = 1$ eV, (f) $V_p = 2$ eV.

the breaking of chemical bonds at the surface as well as an additional potential on the surface atoms. We considered the case where a terminating column was made of copper atoms as well as of oxygen atoms.

In the case that the copper atoms are topmost, the surface bands can be determined from the following equations:

$$g_6(1 - g_3 V_M) + g_{03,06}^2 V_m = 0 \ ,$$
$$g_5(10 - g_2 V_M) + g_{02,05}^2 V_M = 0 \ . \tag{40}$$

Each of Eqs. (40) corresponds to a distinct spin projection, V_M is the additional potential on the surface copper atoms. When writing these equations, we took into account only the nearest-neighbor scattering.

The solutions of Eqs. (40) are given in Fig. 8. These solutions appear in the forbidden gap mainly as a result of the breaking of chemical bonds, and, consequently, they exist even at $V_M = 0$. Deepening the potential has no effect on one of the branches but the other one decreases in energy. The states obtained have a donor character.

In the case where the edge is made of the oxygen atoms, the equality $D = 0$ reduces to

$$g_1(1 - g_5 V_p) + g_{05,01}^2 V_p = 0 \ ,$$
$$g_4(1 - g_6 V_p) + g_{06,04}^2 V_p = 0 \ , \tag{41}$$

where V_p is the additional potential on the surface oxygen atoms. Equations (41) possess a solution if only $V_p > 0$. Figure 8 shows the dependence of these solutions on the wave vector and V_p. From this figure we notice that the obtained states have an acceptor nature. The densities of states in all the surface bands have peculiarities typical of one-dimensional systems. Similar results have been obtained for the (110) edge.[2]

VI. THE POTENTIAL ON SURFACE ATOMS

A. A theory

As above, let us break the crystal up into slabs being parallel with the surface. Then, the potential at the sur-

face can be expressed as the sum over the slabs

$$\Phi(x,y,z) = e\sum_{ij} q_{ij}\Psi(x+x_j,y+y_j,z+z_{ij}) ,\qquad (42)$$

where q_{ij} is the charge of the jth atom in the unit cell of the ith slab, x_j,y_j,z_{ij} are the coordinates of this atom, and e is the electron charge. A plane sublattice contributes to the potential as follows:

$$\Psi(r,z) = \sum_{l}{}' \frac{1}{\sqrt{|r+1|^2+z^2}} + V(z) .\qquad (43)$$

Here $r \equiv (x,y)$, the prime on the sum denotes the absence of the self-interaction of the charges, l is the translation

vector in the slab's plane, and $V(z)$ is the potential of compensating (uniformly distributed) charges in the slab. Entering the last potential is necessary to eliminate the average electrostatic field.

By analogy with the three-dimensional θ transformation of Ewald, we readily obtain for the two-dimensional systems

$$\sum_{l} \exp(-\varepsilon^2|r-l|^2) = \frac{\pi}{\varepsilon^2 S} \sum_{g} \exp\left[igr - \frac{g^2}{4\varepsilon^2}\right] ,\qquad (44)$$

where S is the area of the cell in the ordinary space. By making use of this transformation, we have found

$$\Psi(r,z) = \frac{\pi}{S}\sum_{g\neq 0} e^{igr}\frac{1}{g}\left[e^{zg}\,\mathrm{erfc}\left[\frac{g}{2\lambda}+z\lambda\right] + e^{-zg}\,\mathrm{erfc}\left[\frac{g}{2\lambda}-z\lambda\right]\right]$$
$$+ \sum_{R\neq 0}\frac{\mathrm{erfc}(\lambda R)}{R} - \frac{2\lambda}{\pi^{1/2}}\delta_{z0}\delta_{r0} + \frac{2\pi}{S}z\,\mathrm{erfc}(\lambda z) - \frac{2\pi^{1/2}}{S\lambda}e^{-\lambda^2 z^2} .\qquad (45)$$

The value of the parameter λ must be chosen on the basis of the rapid convergence of both sums (in the ordinary and reciprocal spaces). We have found the value of 0.45 Å^{-1} to be satisfying with this condition.

It should be noted that the method in use can be convenient for the evaluation not only of the potential, but of the electrostatic field and the energies of different extended defects as well. The electrostatic energy can be expressed as

$$\mathcal{E} = \frac{1}{2}\sum_{\alpha} q_\alpha(\Phi_\alpha - \Phi_\alpha^0) ,\qquad (46)$$

where $\Phi_\alpha^0, \Phi_\alpha$ are the electrostatic potentials on the bulk and surface sites, respectively. Sum (46) rapidly converges. Thus, this method gives a convenient mode for evaluating electrostatic energies of twins, grain boundaries, etc. This energy is known to be a major part of the total energy of systems consisting of charged particles.

The method described allows one to calculate the potentials for a crystal lying on a substrate. It is evident that the results depend on which layer is terminating in the substrate.

B. Results of calculations

By way of illustration, let us consider the difference between the potentials in bulk and on different surfaces of La_2CuO_4. Let us suppose that the CuO_2 layer terminates the (001) surface. In this case, we have found that the value of the perturbation potential on the surface copper atom equals -2.3 eV. The potential on the surface oxygen atom is relatively small (-0.3 eV). It follows from these data that, if the CuO_2 layer is topmost, the electronic charge on the surface copper atom is greater than in bulk. The opposite situation occurs if the LaO/CuO_2 sequence of layers is terminating. In this event, the potential on the surface oxygen atoms is relatively large (2.25 eV) and has the positive sign. Thus, the electronic

charge on the surface oxygen atoms would be lower than in bulk.

Apparently, both these two surfaces are not suitable for La_2CuO_4 due to comparatively large potentials on surface atoms. The surface LaO/LaO appears to be more attractive in this connection. The potentials on the surface La (-0.5 eV) and 0 (0.7 eV) atoms are not so large in this case. Note that this surface is usually not conductive. Thus, one can expect that the free surface of La_2CuO_4 is LaO/LaO. It is interesting to note that in all the described cases the perturbation potential sharply decreases with the distance.

In contrast with this, we have found that the values of the potentials on atoms of the (100) surface are too high. Moreover, the potentials on the second and even third layer are large as well, but signs of these potentials alternate. For example, the potential on the surface Cu atom equals 3.7 eV, while it has the value of -3.0 eV on the second layer. It can give rise to dielectric properties of the surface. Another possible consequence could be restructuring of the surface.

The last example is the (110) surface. In this case, if the top of the crystal is made of La, Cu, and O atoms, the potential on the surface Cu atom has the large negative value (-4.3 eV), while the potential on the O(1) atom has the large positive value (4.1 eV). The surface formed by O(2) atoms seems to be more suitable in this case. The potential on the surface oxygen site equals 2.7 eV, while the potential on the copper site in the second layer is -1.5 eV.

We have additionally calculated the dependence of the slab's potential on the distance and found it to be sharply decreasing. It implies that the surface electrostatic potential is very sensitive to the geometry of the surface and, as a consequence, can be explored for searching the best atomic positions. However, in this case, the short-range forces have to be taken into account.

Another possible application of the method described

is as follows. When growing thin films, there is a need to know which layer terminates the film. This is, for example, important for the Josephson-junction construction.[3−8] The choice of the best surface layer, under the condition that relaxation is small, can be based on the minimization of the surface electrostatic energy. Making use of this approach led us to the conclusion that the $LaO/LaO/CuO_2$ sequence of layers terminates the free (001) surface of La_2CuO_4.

Finally, the knowledge of the surface potentials is necessary to determine surface band positions as well as charges on surface atomic sites. For example, we have found that, if the CuO_2 layer terminates the (001) surface, the electronic charge on the surface Cu site increases while, if the LaO layer is topmost, the electronic charge on the surface oxygen site decreases.

VII. CONCLUSIONS

In the present paper we have constructed the simple qualitative model permitting us to elucidate the little understood problem of describing the electronic structure of surfaces of layered copper oxides. We have built the GF of electrons, found the energy dispersion in bands of surface states, obtained the density of electron states in the surface layer, and calculated the potentials on different surfaces of La_2CuO_4. The use of the simplified tight-binding model has made it possible to derive many expressions in an analytical form. We hope the results to be further checked and developed with more precise methods and experiments.

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