

Bound-hole states induced by excess oxygen in $\text{La}_2\text{CuO}_{4+\delta}$

P. Rubin and A. Sherman

Institute of Physics, Estonian Academy of Sciences, Riia 142, EE2400 Tartu, Estonia

(Received 26 July 1995)

Bound-hole states induced by excess oxygen in $\text{La}_2\text{CuO}_{4+\delta}$ are studied in the framework of the extended Hubbard model, with the use of the spin-wave approximation. It is shown that the bound states are subdivided into two groups connected with different perturbations introduced by the excess oxygen in an antiferromagnetically ordered crystal. We interpret the two-band structure of the impurity reflectivity spectrum as a manifestation of these two groups of bound states. Calculated binding energies are in agreement with experiment.

It is well-known that in La_2CuO_4 free carriers appear as a result of rare-earth substitutions or due to excess interstitial oxygen.¹ Along with the creation of free carriers these structure defects induce bound states in the carrier energy spectrum. These states were detected in transport measurements,² the Hall effect,³ and electron-energy-loss spectra.⁴ Of special interest are measurements of the reflectivity spectrum of $\text{La}_2\text{CuO}_{4+\delta}$, carried out in Ref. 5, where two bands in the forbidden gap were observed. At least one of these bands was connected with interstitial oxygen.⁵ To clarify the nature of these two bands we have carried out a theoretical investigation of the bound-hole state with the use of the extended Hubbard model.⁶ This model gives a realistic description of CuO_2 planes where carriers are located.

Lightly doped samples used for measurements of reflectivity spectra⁵ were antiferromagnetically ordered. This ordering has a pronounced effect on bound states that can be most easily seen by the example of a substitutional isoelectronic impurity in the copper position of the CuO_2 plane.⁷ For a given Néel state carriers, which are characterized by a certain value of the z projection of the spin S_z , are mainly located on one magnetic sublattice. We shall call it the “A” sublattice for these carriers, in contrast to the “B” sublattice with a smaller wave-function amplitude. A perturbation produced by the impurity in the copper position resides mainly on one sublattice and thereby influences differently on states on the same, and on the other sublattices. As a consequence, two systems of bound states related to perturbations on the “A” and on the “B” sublattices arise.⁷ For the other Néel state analogous bound states, differences only in the sign of S_z appear. A substitutional isoelectronic impurity in the oxygen position of the CuO_2 plane produces equal perturbations on both sublattices. However, in this case, too, arising bound states can be approximately attributed to perturbations on the “A” and “B” sublattices.⁸

As will be seen below, the considered problem can be also described by a Hamiltonian with equal perturbations on both sublattices of a CuO_2 plane. Thus, mathematical descriptions of bound states induced by an interstitial oxygen and the in-plane isoelectronic oxygen impurity are close. We have found that the observed two-band structure of the impurity reflectivity spectrum is connected with the mentioned two groups of bound states.

The Hamiltonian of the extended Hubbard model can be presented in the form⁹

$$H_0 = \sum_{\mathbf{m}} H_{\mathbf{m}} + 2t\lambda_a \sum_{\mathbf{m}\sigma} (d_{\mathbf{m}\sigma}^\dagger \phi_{\mathbf{m}+\mathbf{a},\sigma} + \text{H.c.}),$$

$$H_{\mathbf{m}} = Un_{\mathbf{m},+1}n_{\mathbf{m},-1} + \Delta \sum_{\sigma} \phi_{\mathbf{m}\sigma}^\dagger \phi_{\mathbf{m}\sigma} + 2t\lambda_0 \sum_{\sigma} (d_{\mathbf{m}\sigma}^\dagger \phi_{\mathbf{m}\sigma} + \text{H.c.}), \quad (1)$$

where $d_{\mathbf{m}\sigma}^\dagger$ is the creation operator of electrons in the $3d_{x^2-y^2}$ orbitals of copper in the plane site \mathbf{m} with spin $\sigma = \pm 1$, $\phi_{\mathbf{m}\sigma}^\dagger$ is the Fourier transform of the operator $\phi_{\mathbf{k}\sigma}^\dagger = (\beta_{\mathbf{k}}/2\sqrt{N}) \sum_{\mathbf{m}\delta} \exp(-i\mathbf{k}\mathbf{m}) p_{\mathbf{m}+\delta,\sigma}^\dagger$, constructed from the creation operators $p_{\mathbf{m}+\delta,\sigma}^\dagger$ of electrons in the $2p_\sigma$ orbitals of oxygen. Complementary linear combinations of these operators, which do not hybridize with the $3d_{x^2-y^2}$ copper orbitals, were omitted in Eq. (1). $\delta = \mathbf{a}/2 = (\pm a/2, 0)$, $(0, \pm a/2)$, where a is the in-plane copper distance, $\beta_{\mathbf{k}} = \{1 + [\cos(k_x a) + \cos(k_y a)]/2\}^{-1/2}$, N is the number of sites; U , Δ , and t are the Hubbard repulsion on copper, the Cu-O promotion energy and hybridization, respectively, $n_{\mathbf{m}\sigma} = d_{\mathbf{m}\sigma}^\dagger d_{\mathbf{m}\sigma}$, $\lambda_{\mathbf{m}} = N^{-1} \sum_{\mathbf{k}} \exp(i\mathbf{k}\mathbf{m}) \beta_{\mathbf{k}}^{-1}$, $\lambda_0 \approx 0.96$, $\lambda_a \approx 0.14$ [other components of $\lambda_{\mathbf{m}}$ are small and the respective terms are omitted in (1)].

An interstitial oxygen ion O^{2-} is positioned above a plane oxygen halfway between two neighboring CuO_2 planes¹⁰ (see Fig. 1). Supposing that the ion is located above

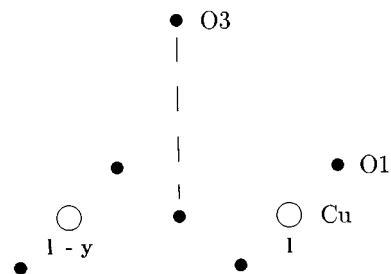


FIG. 1. A part of a Cu-O plane with an excess interstitial oxygen above it. Oxygen and copper ions are shown by filled and open circles, respectively.

the plane oxygen site $\mathbf{l}-\mathbf{y}/2$, we add the following terms in the Hamiltonian:

$$H_i = V_{\text{Cu}}(n_{\mathbf{l}} + n_{\mathbf{l}-\mathbf{y}}) + V_{\text{O}}n_{\mathbf{l}-\mathbf{y}/2}, \quad (2)$$

where $n_{\mathbf{l}} = \sum_{\sigma} n_{\mathbf{l}\sigma}$, $n_{\mathbf{l}-\mathbf{y}/2} = \sum_{\sigma} p_{\mathbf{l}-\mathbf{y}/2, \sigma}^{\dagger} p_{\mathbf{l}-\mathbf{y}/2, \sigma}$, $\mathbf{y} = (0, a)$. By analogy with the Wannier exciton¹¹ the dielectric description with the high-frequency dielectric constant ϵ can be used for potentials V_{Cu} and V_{O} as the distances r_{Cu} and r_{O} between the interstitial ion and the respective plane sites are larger than $(\hbar^2/mE_G)^{1/2} \leq 1 \text{ \AA}$, where $m \sim 10m_0$ is the carrier effective mass¹² and $E_G \approx 2\text{eV}$ is the forbidden gap.¹³ Thus,

$$V_{\text{Cu,O}} = \frac{2e^2}{\epsilon r_{\text{Cu,O}}} \quad (3)$$

[we use the electronic picture in Eq. (2), therefore potentials V_{Cu} and V_{O} are positive]. In notations of Eq. (1) terms (2) can be rewritten as

$$H_i = \sum_{\sigma} V_{\text{O}} \frac{\beta_0^2}{4} (\phi_{\mathbf{l}\sigma}^{\dagger} \phi_{\mathbf{l}\sigma} + \phi_{\mathbf{l}-\mathbf{y}, \sigma}^{\dagger} \phi_{\mathbf{l}-\mathbf{y}, \sigma} + \phi_{\mathbf{l}\sigma}^{\dagger} \phi_{\mathbf{l}-\mathbf{y}, \sigma} + \phi_{\mathbf{l}-\mathbf{y}, \sigma}^{\dagger} \phi_{\mathbf{l}\sigma}) + V_{\text{Cu}}(n_{\mathbf{l}} + n_{\mathbf{l}-\mathbf{y}}), \quad (4)$$

where $\beta_0 \approx 1.29$ is the $\mathbf{m} = \mathbf{0}$ component of the Fourier transform of $\beta_{\mathbf{k}}$ (again we dropped out small terms).

For the low-energy part of the spectrum and for parameters¹⁴ of La_2CuO_4 Hamiltonian (1) can be reduced⁹ to the effective t - J Hamiltonian. This reduction is based on the separation of the Hamiltonian into the one- and two-site parts as indicated in Eq. (1). These two parts are characterized by energy parameters differing by one order of magnitude, that provides an appropriate starting point for the perturbation theory. The zero-order, one-site, part of the Hamiltonian has two sets of states well separated from other states. These states, which correspond to unoccupied and occupied states of the t - J model, can be written in the form

$$|\mathbf{m}2\rangle = \left[c_{21} \frac{1}{\sqrt{2}} (\phi_{\mathbf{m}+1}^{\dagger} d_{\mathbf{m},-1}^{\dagger} - \phi_{\mathbf{m},-1}^{\dagger} d_{\mathbf{m}+1}^{\dagger}) + c_{22} \phi_{\mathbf{m},-1}^{\dagger} \phi_{\mathbf{m}+1}^{\dagger} + c_{23} d_{\mathbf{m},-1}^{\dagger} d_{\mathbf{m}+1}^{\dagger} \right] |v_{\mathbf{m}}\rangle, \\ |\mathbf{m}3\sigma\rangle = [c_{31} \phi_{\mathbf{m}\sigma}^{\dagger} \phi_{\mathbf{m},-\sigma}^{\dagger} d_{\mathbf{m}\sigma}^{\dagger} + c_{32} \phi_{\mathbf{m}\sigma}^{\dagger} d_{\mathbf{m},-\sigma}^{\dagger} d_{\mathbf{m}\sigma}^{\dagger}] |v_{\mathbf{m}}\rangle, \quad (5)$$

where $|v_{\mathbf{m}}\rangle$ is the site vacuum state and the coefficients c_{ij} are obtained in the course of the diagonalization of $H_{\mathbf{m}}$ [recall that besides (5) there are two other occupied oxygen states which do not hybridize with copper; thus, the unoccupied and occupied states of the t - J model correspond to four- and five-electron site states of the Hubbard model, respectively]. Omitting unessential terms, Hamiltonians (1) and (4) can be rewritten in terms of state vectors (5)

$$H_0 = t_{\text{eff}} \sum_{\mathbf{m}\mathbf{a}\sigma} |\mathbf{m}+\mathbf{a}, 3\sigma\rangle \langle \mathbf{m}+\mathbf{a}, 2| |\mathbf{m}2\rangle \langle \mathbf{m}3\sigma| + \frac{J}{2} \sum_{\mathbf{m}\mathbf{a}} \mathbf{S}_{\mathbf{m}} \cdot \mathbf{S}_{\mathbf{m}+\mathbf{a}}, \quad (6)$$

$$H_i = \sum_{\mathbf{l}'} \epsilon |\mathbf{l}'2\rangle \langle \mathbf{l}'2|, \quad (7)$$

where

$$S_{\mathbf{m}}^{\sigma} = S_{\mathbf{m}}^x + i\sigma S_{\mathbf{m}}^y = |\mathbf{m}3\sigma\rangle \langle \mathbf{m}3, -\sigma|,$$

$$S_{\mathbf{m}}^z = \frac{1}{2} \sum_{\sigma} \sigma |\mathbf{m}3\sigma\rangle \langle \mathbf{m}3\sigma|,$$

are the components of the spin operator $\mathbf{S}_{\mathbf{m}}$,

$$\epsilon = \frac{V_{\text{O}}\beta_0^2}{4} (2c_{22}^2 + c_{21}^2 - 2c_{31}^2 - c_{32}^2) + V_{\text{Cu}}(c_{21}^2 + 2c_{23}^2 - c_{31}^2 - 2c_{32}^2),$$

$\mathbf{l}' = \mathbf{l}, \mathbf{l}-\mathbf{y}$, and t_{eff} and J are the effective hopping and superexchange constants, respectively (in terms of the coefficients c_{ij} and site energies these constants are given in Ref. 9).

Further simplifications of Hamiltonians (6) and (7) can be achieved with the use of the spin-wave approximation^{15,16} which has been shown to be remarkably accurate in the description of undoped and lightly doped samples as mean numbers of magnons are usually small.^{16,17} The approximation reduces to neglecting terms of the third and higher orders in the spin-wave operators $b_{\mathbf{m}}$ introduced in Eq. (6) by the formulas

$$S_{\mathbf{m}}^{+1} = \Phi_{\mathbf{m}} b_{\mathbf{m}} P_{\mathbf{m}}^{+1} + b_{\mathbf{m}}^{\dagger} \Phi_{\mathbf{m}} P_{\mathbf{m}}^{-1}, \quad S_{\mathbf{m}}^{-1} = (S_{\mathbf{m}}^{+1})^{\dagger}, \\ \Phi_{\mathbf{m}} = \sqrt{1 - b_{\mathbf{m}}^{\dagger} b_{\mathbf{m}}}, \quad S_{\mathbf{m}}^z = e^{i\Pi\mathbf{m}} \left(\frac{n_{\mathbf{m}}}{2} - b_{\mathbf{m}}^{\dagger} b_{\mathbf{m}} \right),$$

where $\Pi = (\pi/a, \pi/a)$, $P_{\mathbf{m}}^{\sigma} = [1 + \sigma \exp(i\Pi\mathbf{m})]/2$.

Let us introduce the hole creation operator $h_{\mathbf{m}}^{\dagger} = \sum_{\sigma} P_{\mathbf{m}}^{\sigma} |\mathbf{m}2\rangle \langle \mathbf{m}3\sigma|$ for the Néel state $|\mathcal{N}\rangle = \Pi_{\mathbf{m}} (\sum_{\sigma} P_{\mathbf{m}}^{\sigma} |\mathbf{m}3\sigma\rangle)$ (the second Néel state and the respective hole operator can be obtained by substituting $P_{\mathbf{m}}^{\sigma}$ with $1 - P_{\mathbf{m}}^{\sigma}$ in these formulas). After the unitary transformation¹⁶ which diagonalizes the spin part of the Hamiltonian, it reads

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_i \\ = t_{\text{eff}} \sum_{\mathbf{m}\mathbf{m}'\mathbf{a}} [h_{\mathbf{m}+\mathbf{a}} h_{\mathbf{m}}^{\dagger} b_{\mathbf{m}-\mathbf{m}'}^{\dagger} (u_{\mathbf{m}'+\mathbf{a}} + v_{\mathbf{m}'}) + \text{H.c.}] + \frac{J}{2} \sum_{\mathbf{m}\mathbf{m}'} \omega_{\mathbf{m}} b_{\mathbf{m}}^{\dagger} b_{\mathbf{m}+\mathbf{m}'} + \epsilon (\tilde{n}_{\mathbf{l}} + \tilde{n}_{\mathbf{l}-\mathbf{y}}), \quad (8)$$

where $u_{\mathbf{m}}, v_{\mathbf{m}}$ and $\omega_{\mathbf{m}}$ are the Fourier transforms of $\cosh(\alpha_{\mathbf{k}})$, $-\sinh(\alpha_{\mathbf{k}})$, and $\omega_{\mathbf{k}} = 4\sqrt{1 - \gamma_{\mathbf{k}}^2}$, respectively, $\alpha_{\mathbf{k}} = (1/8) \ln[(1 + \gamma_{\mathbf{k}})/(1 - \gamma_{\mathbf{k}})]$, $\gamma_{\mathbf{k}} = [\cos(k_x a) + \cos(k_y a)]/2$, $\tilde{n}_{\mathbf{l}} = h_{\mathbf{l}}^{\dagger} h_{\mathbf{l}}$. Due to the fast decrease of $u_{\mathbf{m}'+\mathbf{a}} + v_{\mathbf{m}'}$ and $\omega_{\mathbf{m}'}$ with the growth of $|\mathbf{m}'|$, only the components with $\mathbf{m}' = (\pm a, 0), (0, \pm a)$ for the sum in the first, kinetic energy term and components with $\mathbf{m}' = (0, 0), (\pm a, \pm a), (\pm 2a, 0), (0, \pm 2a)$ for $\omega_{\mathbf{m}'}$ in the second, magnetic energy term will be retained in Eq. (8) in subsequent calculations (before the unitary transformation the kinetic term has only an addend with $\mathbf{m}' = -\mathbf{a}$ [see Eq. (8)] and the magnetic energy term is

comprised of one-site and nearest-neighbor addends; the unitary transformation, which takes into account transversal spin fluctuations, does not significantly increase the ranges of these interactions). The eigenstates are characterized by the value of S_z . In the considered case $J/t_{\text{eff}} \geq 0.2$, the lowest eigenstates of \mathcal{H}_0 correspond to $S_z = \pm 1/2$ and can be approximately presented in the form¹⁶

$$|\mathbf{k}\rangle = \sqrt{\frac{2}{N}} \sum_{\mathbf{L}} e^{i\mathbf{k}\mathbf{L}} \left[c_{0\mathbf{k}} h_{\mathbf{L}}^\dagger + \frac{c_{1\mathbf{k}} t_{\text{eff}}}{V_{\mathbf{k}}} \right. \\ \left. \times \sum_{\mathbf{a}, \mathbf{b}} e^{i\mathbf{k}(\mathbf{a}+\mathbf{b})} (u_{\mathbf{a}+\mathbf{b}} + v_{\mathbf{b}}) b_{\mathbf{L}}^\dagger h_{\mathbf{L}+\mathbf{b}}^\dagger \right] |\mathcal{N}\rangle, \quad (9)$$

where the summation over \mathbf{L} proceeds over sites of one sublattice (in dependence on the selected sublattice S_z equals $1/2$ or $-1/2$),

$$c_{0\mathbf{k}} = \left[1 + \left(\frac{V_{\mathbf{k}}}{\varepsilon_{\mathbf{k}} - E_{\mathbf{k}}} \right)^2 \right]^{-1/2}, \quad c_{1\mathbf{k}} = \frac{V_{\mathbf{k}}}{\varepsilon_{\mathbf{k}} - E_{\mathbf{k}}} c_{0\mathbf{k}}, \\ \varepsilon_{\mathbf{k}} = \frac{E_{\mathbf{k}}}{2} - \sqrt{\frac{1}{4} E_{\mathbf{k}}^2 + V_{\mathbf{k}}^2},$$

$$E_{\mathbf{k}} = \frac{J}{2} \frac{t_{\text{eff}}^2}{V_{\mathbf{k}}^2} \sum_{\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{m}} \cos[\mathbf{k}(\mathbf{a}-\mathbf{b})] (u_{\mathbf{a}+\mathbf{c}} + v_{\mathbf{c}}) \\ \times (u_{\mathbf{b}+\mathbf{c}-\mathbf{m}} + v_{\mathbf{c}-\mathbf{m}}) \omega_{\mathbf{m}},$$

$$V_{\mathbf{k}}^2 = t_{\text{eff}}^2 \sum_{\mathbf{a}, \mathbf{b}, \mathbf{c}} \cos[\mathbf{k}(\mathbf{a}-\mathbf{b})] (u_{\mathbf{a}+\mathbf{c}} + v_{\mathbf{c}}) (u_{\mathbf{b}+\mathbf{c}} + v_{\mathbf{c}}),$$

$\varepsilon_{\mathbf{k}}$ is the eigenvalue corresponding to $|\mathbf{k}\rangle$, the wave vector \mathbf{k} belongs to the magnetic Brillouin zone, and $\mathbf{a}, \mathbf{b}, \mathbf{c} = (\pm a, 0), (0, \pm a)$.

In Eq. (9) $|c_{0\mathbf{k}}|^2 \gg |c_{1\mathbf{k}}|^2$. Thus, in the state $|\mathbf{k}\rangle$ the hole is mainly located on the sublattice labeled by the index \mathbf{L} . This sublattice is the “A” sublattice for the given state $|\mathbf{k}\rangle$, while the complementary sublattice is the “B” one. If the site \mathbf{L} in \mathcal{H}_i belongs to the “A” sublattice, the site $\mathbf{l}-\mathbf{y}$ is of the “B” sublattice. Thus, as mentioned above, the impurity Hamiltonian contains two equal terms corresponding to perturbations on both sublattices.

Since the band formed by states (9) is well separated from other bands with $S_z = \pm 1/2$,¹⁶ the bound states are mainly constructed from states (9). In this case the equation for the bound states reads

$$\det(I + 2\pi G^0 W) = 0, \quad (10)$$

where I is the unit matrix,

$$G_{\mathbf{L}\mathbf{L}'}^0(E) = \frac{2}{(2\pi)^3} \int d\mathbf{k} e^{i\mathbf{k}(\mathbf{L}-\mathbf{L}')} \frac{1}{(E - \varepsilon_{\mathbf{k}})}$$

is the unperturbed Green’s function (the integration is performed over the magnetic Brillouin zone),

$$W_{\mathbf{L}\mathbf{L}'} = -\epsilon \langle \mathbf{L} | (\tilde{n}_{\mathbf{l}} + \tilde{n}_{\mathbf{l}-\mathbf{y}}) | \mathbf{L}' \rangle,$$

$|\mathbf{L}\rangle$ is the Wannier function built from states (9), and the indices \mathbf{L} and \mathbf{L}' run over sites of the same magnetic sublattice as in function (9).

Weak dependences of $c_{0\mathbf{k}}, c_{1\mathbf{k}}$, and $V_{\mathbf{k}}$ on \mathbf{k} can be neglected and these quantities can be approximated by their values at $\mathbf{k} = (\mp \pi/2a, \mp \pi/2a)$, where the minimum of $\varepsilon_{\mathbf{k}}$ is situated at $J/t_{\text{eff}} \geq 0.2$.¹⁶ We denote these values with c_0, c_1 and V . In this approximation,

$$W_{\mathbf{L}\mathbf{L}'} = -\epsilon c_0^2 \delta_{\mathbf{L},\mathbf{l}} \delta_{\mathbf{L}\mathbf{L}'} - \epsilon \frac{t_{\text{eff}}^2}{V^2} c_1^2 \sum_{\mathbf{a}, \mathbf{b}, \mathbf{c}} (u_{\mathbf{a}+\mathbf{b}} + v_{\mathbf{b}}) \\ \times (u_{\mathbf{c}+\mathbf{b}} + v_{\mathbf{b}}) \delta_{\mathbf{L},\mathbf{l}-\mathbf{y}+\mathbf{a}} \delta_{\mathbf{L}-\mathbf{a},\mathbf{L}'-\mathbf{c}}.$$

Two terms in the right-hand side of this equation are connected with the perturbations produced by the interstitial oxygen on the “A” and “B” sublattices, respectively.

After the unitary transformation with the matrix

$$S = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1/\sqrt{2} & 0 & 1/\sqrt{2} \\ 0 & 0 & 1 & 0 \\ 0 & 1/\sqrt{2} & 0 & -1/\sqrt{2} \end{pmatrix},$$

Eq. (10) splits into two equations

$$1 + 2\pi(G_{11}^0 - G_{13}^0)(W_{22} - W_{13}) = 0, \quad (11)$$

$$\det \left[2\pi \begin{pmatrix} G_{11}^0 & G_{12}^0 \sqrt{2} & G_{13}^0 \\ G_{12}^0 \sqrt{2} & G_{11}^0 + G_{13}^0 & G_{12}^0 \sqrt{2} \\ G_{13}^0 & G_{12}^0 \sqrt{2} & G_{11}^0 \end{pmatrix} \right. \\ \left. \times \begin{pmatrix} W_{11} & W_{12} \sqrt{2} & W_{13} \\ W_{12} \sqrt{2} & W_{22} + W_{13} & W_{12} \sqrt{2} \\ W_{13} & W_{12} \sqrt{2} & W_{22} \end{pmatrix} + I \right] = 0 \quad (12)$$

for bound states belonging to the A'' and A' representations of the C_s group, respectively. In Eqs. (11) and (12) sites $\mathbf{l}, \mathbf{l}-\mathbf{y}+\mathbf{x}, \mathbf{l}-2\mathbf{y}$, and $\mathbf{l}-\mathbf{y}-\mathbf{x}$ are denoted by numbers 1 to 4, correspondingly.

As mentioned, the perturbation on the “A” sublattice $\sim \epsilon c_0^2$ is contained in the matrix element W_{11} only, and $|W_{11}| \gg |W_{12}|, |W_{13}|, |W_{22}|$. Besides, $|G_{11}^0| \gg |G_{12}^0|, |G_{13}^0|$ in the considered energy interval. As a consequence, Eq. (12) can be approximately rewritten in a block-diagonal form by neglecting nondiagonal elements in the first row and column of the matrices [the validity of this approximation, which is conditioned by large energy and configuration differences of the respective states, was verified by comparing with exact solutions of Eq. (12)]. Thus, Eq. (12) splits into two equations. One of these equations describes a bound state connected with the perturbation on the “A” sublattice and the other equation is for two bound states due to the perturbation on the “B” sublattice. We denote these states as A'_1 and A'_2, A'_3 , respectively. As can be seen from Eq. (11), the level A'' is determined by the perturbation on the “B” sublattice.

For parameters¹⁴ of La_2CuO_4 the ratio J/t_{eff} can be estimated to lie in the range 0.2–0.5. For some values in this range calculated energies of the states A'' , A'_1 , and A'_2 , counted from the bottom of the band $\varepsilon(\mathbf{k})$, are listed in Table I. The high-frequency dielectric constant⁵ $\varepsilon_\infty = 5$ was used in these calculations. The A'_3 level is split off the band bottom only at large perturbations and therefore is not considered here.

TABLE I. Bound level energies in dependence on the ratio J/t_{eff} .

J/t_{eff}	$\Delta E, \text{eV}$		
	A''	A'_2	A'_1
0.214	0.063	0.066	0.467
0.275	0.059	0.063	0.472
0.421	0.053	0.056	0.492

As follows from Table I, the levels A'' and A'_2 , which appear due to the perturbation on the “ B ” sublattice, are close in energy. The A'_1 level, connected with the perturbation on the “ A ” sublattice, is much more deep. Thus, one can speak about two groups of bound states connected with different perturbations and well separated in energy.

We can identify these two groups of bound states with two bands observed⁵ in reflectivity spectra of $\text{La}_2\text{CuO}_{4+\delta}$ at 0.13 and 0.5 eV. These values contain a contribution of the polaronic effect that apparently comprises the main part of the difference between the observed positions of the reflectivity bands and the binding energies in Table I. These energies were obtained in the rigid lattice, i.e., without considering the polaronic effect. We note that the simple dielectric

description for this effect is inapplicable in the considered case. The binding energy of the levels, without a polaronic contribution, can be obtained from measurements of the Hall effect. For the band at 0.13 eV this energy was found³ to be 0.035 eV which is close to the values given in Table I for the A'' and A'_2 levels. Thus, the polaronic shift can be approximately estimated as 0.08 eV. The differences between the position of the second band, 0.5 eV, and the binding energies of the A'_1 level in Table I are also close to this value.

Analogously two sets of qualitatively different bound states can be expected to appear also for other impurities. Since these two sets are conditioned by the antiferromagnetic order, they can serve as its indicator.

In summary, we calculated level energies of bound-hole states induced by excess oxygen in $\text{La}_2\text{CuO}_{4+\delta}$. These levels were shown to be subdivided into two groups connected with perturbations on the “ A ” and “ B ” sublattices and well separated in energy. The first of these groups consists of the A'_1 level and the second one, of the closely spaced A'' and A'_2 levels. We identified these two groups of levels with two bands observed in the reflectivity spectra of $\text{La}_2\text{CuO}_{4+\delta}$ at 0.5 and 0.13 eV, respectively. Calculated binding energies of the levels are in agreement with experiment.

This work was supported by the Estonian Science Foundation under Grants Nos. ETF-67 and ETF-349.

- ¹J. T. Markert, Y. Dalichaouch, and M. B. Maple, in *Physical Properties of High Temperature Superconductors*, edited by D. M. Ginsberg (World Scientific, Singapore, 1989), Vol. 1, p. 265.
- ²M. F. Hundley *et al.*, *Physica C* **172**, 455 (1991).
- ³N. W. Preyer *et al.*, *Phys. Rev. B* **39**, 11 563 (1989).
- ⁴H. Romberg *et al.*, *Phys. Rev. B* **42**, 8768 (1990).
- ⁵J. P. Falck *et al.*, *Phys. Rev. B* **48**, 4043 (1993).
- ⁶V. J. Emery, *Phys. Rev. Lett.* **58**, 2794 (1987).
- ⁷P. Rubin and A. Sherman, *Phys. Status Solidi B* **166**, 161 (1991).
- ⁸A. Sherman and P. Rubin, *Solid State Commun.* **86**, 23 (1993).
- ⁹A. V. Sherman, *Phys. Rev. B* **47**, 11 521 (1993); *Physica C* **211**, 329 (1993).
- ¹⁰F. Izumi *et al.*, *Physica C* **235-240**, 841 (1994).

- ¹¹R. S. Knox, *Theory of Excitons* (Academic, New York, 1963).
- ¹²M. Schreiber, J. Sabczynski, and A. Sherman, *Philos. Mag. B* **65**, 881 (1992).
- ¹³N. M. Plakida, *High-Temperature Superconductivity* (Springer-Verlag, Berlin, 1995).
- ¹⁴A. K. McMahan *et al.*, *Phys. Rev. B* **42**, 6268 (1990).
- ¹⁵S. Schmitt-Rink, C. M. Varma, and A. E. Ruckenstein, *Phys. Rev. Lett.* **60**, 2793 (1988).
- ¹⁶A. V. Sherman, *Solid State Commun.* **76**, 321 (1990); *Physica C* **171**, 395 (1990).
- ¹⁷A. Ramšak and P. Horsch, *Phys. Rev. B* **48**, 10 559 (1993); D. A. Huse, *ibid.* **37**, 2380 (1988); S. Chakravarty, B. I. Halperin, and D. R. Nelson, *ibid.* **39**, 2344 (1989).