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Localized hole states in $La_2CuO_{4+\delta}$

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Bound hole states induced by excess oxygen in $La_2CuO_{4+\delta}$ 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. Along with the creation of free carriers these structure defects induce bound states in the carrier energy spectrum. These states were detected in different experiments [1]. Of special interest are measurements of the reflectivity spectrum of $La_2CuO_{4+\delta}$, carried out in Ref. 2, where two bands were observed in the forbidden gap. 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. This model gives a realistic description of the CuO_2 planes where carriers are located.

Lightly doped samples used for measurements of reflectivity spectra [2] were ordered antiferromagnetically. 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 [3]. 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 «own» sublattice for these carriers, in contrast to the «alien» 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 states on the same, and on the other sublattices. As a consequence, two systems of bound states related to perturbations on the «own» and on the «alien» sublattices arise [3]. For the other Néel state, analogous bound states, appear differing only in the sign of S_z. A substitutional isoelectronic impurity in the oxygen position of the CuO_2 plane produces equal perturbations on both sublattices. However, in this case, too, the arising bound states can be attributed approximately to perturbations on the «own» and «alien» sublattices [4].

As will be seen below, the considered problem can also be described by a Hamiltonian with equal perturbations on both sublattices of the CuO_2 plane. Thus, the mathematical descriptions of bound states induced by an interstitial oxygen and by 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 form [5]

$$H_0 = \sum_{\mathrm{m}} H_{\mathrm{m}} + 2t\lambda_a \sum_{\mathrm{m}a\sigma} \left(d^+_{\mathrm{m}\sigma} \varphi_{\mathrm{m+a},\sigma} + \mathrm{H.c.} \right),$$

$$H_{\mathrm{m}} = U n_{\mathrm{m},+1}\, n_{\mathrm{m},-1} + \Delta \sum_{\sigma} \varphi^+_{\mathrm{m}\sigma} \varphi_{\mathrm{m}\sigma} + \qquad (1)$$

$$+ 2t\lambda_0 \sum_{\sigma} \left(d^+_{\mathrm{m}\sigma} \varphi_{\mathrm{m}\sigma} + \mathrm{H.c.} \right),$$

where $d^+_{\mathrm{m}\sigma}$ is the creation operator of electrons in the $3d_{x^2-y^2}$ orbitals of copper in the plane site m with spin $\sigma = \pm 1$, $\varphi^+_{\mathrm{m}\sigma}$ is the Fourier transform of the operator

$$\varphi^+_{\mathrm{k}\sigma} = \left(\beta_{\mathrm{k}} / 2\sqrt{N} \right) \sum_{\mathrm{m}\vec{\delta}} \exp(-i\mathrm{km})\, p^+_{\mathrm{m}+\vec{\delta},\sigma},$$

constructed from the creation operators $p^+_{\mathrm{m}+\vec{\delta},\sigma}$ 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). $\vec{\delta} = \mathrm{a}/2 = (\pm a/2, 0), (0, \pm a/2)$, where a is the in-plane copper distance,

$$\beta_{\mathrm{k}} = \left\{ 1 + \left[\cos(k_x a) + \cos(k_y a) \right] / 2 \right\}^{-1/2};$$

N is the number of sites; U, Δ and t are the Hubbard repulsion on copper, the Cu-O promotion energy and hybridization, respectively; $n_{\mathrm{m}\sigma} = d^+_{\mathrm{m}\sigma} d_{\mathrm{m}\sigma}$,

$$\lambda_{\mathrm{m}} = N^{-1} \sum_{\mathrm{k}} \exp(i\mathrm{km})\, \beta_{\mathrm{k}}^{-1} ,$$

$\lambda_0 \approx 0.96$, $\lambda_{\mathrm{a}} \approx 0.14$ [other components of λ_{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 planes [6]. Supposing that the ion is located above the plane oxygen site $\mathrm{l} - \mathrm{y}/2$, we add the following terms to the Hamiltonian:

$$H_i = V_{\mathrm{Cu}}\left(n_{\mathrm{l}} + n_{\mathrm{l-y}}\right) + V_{\mathrm{O}} n_{\mathrm{l-y/2}} , \qquad (2)$$

where

$$n_{\mathrm{l}} = \sum_{\sigma} n_{\mathrm{l}\sigma} , \quad n_{\mathrm{l-y/2}} = \sum_{\sigma} p^{+}_{\mathrm{l-y/2},\sigma} p_{\mathrm{l-y/2},\sigma} ,$$

$\mathrm{y} = (0, a)$. By analogy with the Wannier exciton 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 $(\hbar^2/mE_G)^{1/2} \leq 1$ Å, where $m \sim 10m_0$ is the carrier effective mass [7] and $E_G \approx 2$ eV is the forbidden gap. Thus,

$$V_{\mathrm{Cu,O}} = \frac{2e^2}{\varepsilon r_{\mathrm{Cu,O}}} \qquad (3)$$

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

$$H_i = \sum_{\sigma} V_{\mathrm{O}} \frac{\beta_0^2}{4} \left(\varphi^{+}_{\mathrm{l}\sigma} \varphi_{\mathrm{l}\sigma} + \varphi^{+}_{\mathrm{l-y},\sigma} \varphi_{\mathrm{l-y},\sigma} + \varphi^{+}_{\mathrm{l}\sigma} \varphi_{\mathrm{l-y},\sigma} + \varphi^{+}_{\mathrm{l-y},\sigma} \varphi_{\mathrm{l}\sigma}\right) + V_{\mathrm{Cu}}\left(n_{\mathrm{l}} + n_{\mathrm{l-y}}\right) , \qquad (4)$$

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

For the low-energy part of the spectrum and for parameters of La_2CuO_4 [8] Hamiltonian (1) can be reduced [5] 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 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

$$|\mathrm{m}2\rangle = \left[c_{21} \frac{1}{\sqrt{2}} \left(\varphi^{+}_{\mathrm{m},+1}\, d^{+}_{\mathrm{m},-1} - \varphi^{+}_{\mathrm{m},-1}\, d^{+}_{\mathrm{m},+1}\right) + c_{22} \varphi^{+}_{\mathrm{m},-1}\, \varphi^{+}_{\mathrm{m},+1} + c_{23} d^{+}_{\mathrm{m},-1}\, d^{+}_{\mathrm{m},+1}\right] |v_{\mathrm{m}}\rangle ,$$

$$|\mathrm{m}3\sigma\rangle = \left[c_{31} \varphi^{+}_{\mathrm{m}\sigma}\, \varphi^{+}_{\mathrm{m},-\sigma}\, d^{+}_{\mathrm{m}\sigma} + c_{32} \varphi^{+}_{\mathrm{m}\sigma}\, d^{+}_{\mathrm{m},-\sigma}\, d^{+}_{\mathrm{m}\sigma}\right] |v_{\mathrm{m}}\rangle , \qquad (5)$$

where $|v_{\mathrm{m}}\rangle$ is the site vacuum state and the coefficients c_{ij} are obtained in the course of the diagonalization of H_{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)

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

$$H_i = \sum_{\mathrm{l'}} \varepsilon |\mathrm{l'}2\rangle\langle \mathrm{l'}2| , \qquad (7)$$

where

$$S^{\sigma}_{\mathrm{m}} = S^{x}_{\mathrm{m}} + i\sigma S^{y}_{\mathrm{m}} = |\mathrm{m}3\sigma\rangle\langle \mathrm{m}3,-\sigma| , S^{z}_{\mathrm{m}} = \frac{1}{2} \sum_{\sigma} \sigma |\mathrm{m}3\sigma\rangle\langle \mathrm{m}3\sigma| ,$$

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

$$\varepsilon = \frac{V_O \beta_0^2}{4}\left(2c_{22}^2 + c_{21}^2 - 2c_{31}^2 - c_{32}^2\right) +$$

$$+ V_{Cu}\left(c_{21}^2 + 2c_{23}^2 - c_{31}^2 - 2c_{32}^2\right) ;$$

$\mathrm{l}' = \mathrm{l}, \mathrm{l} - \mathrm{y}$, 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. 5).

Further simplifications of Hamiltonians (6) and (7) can be achieved with the use of the spin-wave approximation which has been shown to be remarkably accurate in the description of undoped and lightly doped samples. The approximation amounts to a neglect of terms of third and higher orders in the spin-wave operators $b_{\mathbf{m}}$, introduced in Eq. (6) by the formulas

$$S_{\mathbf{m}}^{+1} = \Phi_{\mathbf{m}}\, b_{\mathbf{m}}\, P_{\mathbf{m}}^{+1} + b_{\mathbf{m}}^{+}\, \Phi_{\mathbf{m}}\, P_{\mathbf{m}}^{-1} ,$$

$$S_{\mathbf{m}}^{-1} = (S_{\mathbf{m}}^{+1})^{+} , \quad \Phi_{\mathbf{m}} = \sqrt{1 - b_{\mathbf{m}}^{+} b_{\mathbf{m}}} ,$$

$$S_{\mathbf{m}}^{z} = \exp(i\Pi\cdot\mathbf{m}) \left(\frac{n_{\mathbf{m}}}{2} - b_{\mathbf{m}}^{+} b_{\mathbf{m}}\right) ,$$

where

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

Let us introduce the hole creation operator

$$h_{\mathbf{m}}^{+} = \sum_{\sigma} P_{\mathbf{m}}^{\sigma} |\mathbf{m}2\rangle\langle \mathbf{m}3\sigma|$$

for the Néel state

$$|N\rangle = \Pi_{\mathbf{m}} \sum_{\sigma} P_{\mathbf{m}}^{\sigma} |\mathbf{m}3\sigma\rangle$$

(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 transformation [9] which diagonalizes the spin part of the Hamiltonian, it reads

$$H' = H_0' + H_i' =$$

$$= t_{\mathrm{eff}} \sum_{\mathbf{mm'a}} \left[h_{\mathbf{m+a}}\, h_{\mathbf{m}}^{+}\, b_{\mathbf{m-m'}}^{+} \left(u_{\mathbf{m'+a}} + v_{\mathbf{m'}}\right) + \mathrm{H.c.}\right] +$$

$$+ \frac{J}{2} \sum_{\mathbf{mm'}} \omega_{\mathbf{m'}}\, b_{\mathbf{m}}^{+}\, b_{\mathbf{m+m'}} + \varepsilon\left(\tilde{n}_{\mathrm{l}} + \tilde{n}_{\mathrm{l-y}}\right) , \qquad (8)$$

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, $\alpha_{\mathbf{k}} = 1/8 \ln[(1 + \gamma_{\mathbf{k}})/(1 - \gamma_{\mathbf{k}})]$, $\gamma_{\mathbf{k}} = [\cos(k_x a) + \cos(k_y a)]/2$, $\tilde{n}_{\mathrm{l}} = h_{\mathrm{l}}^{+} h_{\mathrm{l}}$. Due to the fast decrease of $u_{\mathbf{m'+a}} + v_{\mathbf{m'}}$ 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. If the site l in H_i' belongs to the «own» sublattice, the site l − y is of the «alien» sublattice. Thus, as mentioned above, the impurity Hamiltonian contains two equal terms corresponding to perturbations on both sublattices.

The equation for the bound states reads

$$\det\left(I - (E - H_0')^{-1} H_i'\right) = 0 , \qquad (9)$$

where I is the unit matrix and E is the energy of the bound state.

We solved Eq. (9) in the subspace of states forming the lowest band of H_0'. For $J/t_{\mathrm{eff}} \geq 0.2$ these states correspond to $S_z = \pm 1/2$ and can be written approximately in the form [9]

$$|\mathbf{k}\rangle = \sqrt{2/N} \sum_{\mathrm{L}} \exp(i\mathbf{k}\mathrm{L}) \left[c_{0\mathbf{k}}\, h_{\mathrm{L}}^{+} + c_{1\mathbf{k}} \sum_{\mathbf{a,a'}} \exp\left(i\mathbf{k}(\mathbf{a} + \mathbf{a}')\right) \left(u_{\mathbf{a+a'}} + v_{\mathbf{a'}}\right) b_{\mathrm{L}}^{+}\, h_{\mathrm{L+a'}}^{+}\right] |N\rangle , \qquad (10)$$

where $|c_{0\mathbf{k}}| \gg |c_{1\mathbf{k}}|$ and the summation over L proceeds over sites of one («own») sublattice.

After the unitary transformation Eq. (9) splits into two equations for bound states belonging to the A' and A'' representations of the C_s group, respectively. We denote corresponding states as A_1', A_2', A_3', and A''. It can be shown that the A_2', A_3', and A'' are connected mainly with the perturbation on the «alien» sublattice and the A_1' level is due to the perturbation on the «own» sublattice.

For parameters of La_2CuO_4 [8] the ratio J/t_{eff} can be estimated to lie in the range 0.2–0.5. Calculated energies of the states A'', A_1', and A_2', counted from the bottom of the band Eq. (10), are listed in Table for some values in this range. The high-frequency dielectric constant $\varepsilon_\infty = 5$ [2] 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.

As follows from Table, the levels A'' and A_2', which appear due to the perturbation on the «alien» sublattice, are close in energy. The A_1' level, connected with the perturbation on the «own» sublattice, is much deeper. Thus, one can speak about two groups of bound states connected with different perturbations and well separated in energy.

Table

Bound level energies as a function of the ratio J/t_{eff}

J/T_{eff}	ΔE, 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

We can identify these two groups of bound states with two bands observed [2] in reflectivity spectra of $La_2CuO_{4+\delta}$ 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. 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 found [2] to be 0.035 eV which is close to the values given in Table 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 are also close to this value.

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