Chain-oxygen vacancy model of the F^+ centre in $YBa_2Cu_3O_{6+x}$

LETTER TO THE EDITOR

Chain-oxygen vacancy model of the F$^+$ centre in YBa$_2$Cu$_3$O$_{6+x}$

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Abstract. By using the Green's function method, the localized state energy for an electron trapped in the chain-oxygen vacancy in YBa$_2$Cu$_3$O$_{6+x}$ has been calculated. At reasonable parameter values it lies above the chain- and plane-oxygen band top. Correspondingly the formation of a stable chain F$^+$ centre can be supposed, as in the mechanism (Federici J F *et al* 1995 *Phys. Rev.* B **52** 15 592) of photoinduced conductivity.

The properties of the new high-temperature oxide superconductors are greatly determined and influenced by defects and local distortions. Oxygen stoichiometry plays an especially decisive role. In [1], a calculation of the F$^+$ centre in the CuO$_2$ plane of these systems has been made, considering the centre as an electron mainly trapped in the inner region of the oxygen vacancy. Stability of the F$^+$ centre has been demonstrated, and the localized state energy as a function of vacancy-orbital and nearest oxygen p-orbital transfer integral has been obtained.

   In this letter we present the results of an analogous calculation for the F$^+$ centre in the chain of the YBa$_2$Cu$_3$O$_{6+x}$ system using the model of an O(1)-vacancy-trapped electron. The possibility of formation and stabilization of such centres is essential from the point of view of the charge transfer model [2] of the photoinduced persistent conductivity and superconductivity of YBa$_2$Cu$_3$O$_{6+x}$. Illumination of films of this material generates electron–hole pairs. The electrons are trapped [2] at the oxygen vacancies in the CuO chains, remaining spatially separated from the holes residing in the superconductivity playground CuO$_2$ planes. Release of the electrons from these traps quenches the effect. Our present calculation confirms the possibility of electron trapping at the chain-oxygen vacancy.

   We calculate the defect electron levels by the well known Green's function method. The unperturbed electron spectrum is modelled by the oxygen chain-strip bands formed by direct overlap of the O(1) and O(4,apex) 2p orbitals oriented along the lines joining these ions:

$$\epsilon_1 = \epsilon_p$$
$$\epsilon_{2,3} = \epsilon_p \pm [2(\langle pp\sigma\rangle^2 + \langle pp\pi\rangle^2 + 2\langle pp\sigma\rangle\langle pp\pi\rangle \cos k_x a)]^{1/2}. \tag{1}$$

Here the transfer integrals are taken, according to [3], to be the same as in [1]: $\langle pp\sigma\rangle = 1.0$ eV and $\langle pp\pi\rangle = -0.3$ eV; a is the O(1)–O(1) distance in the chain and we take for simplicity the distances Cu(1)–O(1) and Cu(1)–O(4) to be equal. The width of the band is 3.68 eV and it lies between the copper Hubbard subbands. As projected onto the CuO$_2$ plane-oxygen band, the upper chain band edge lies at 0.4 eV below the top of the plane band.

The bare O^{2-} 2p-state energies (ϵ_p) in the crystal have been calculated by the Watson approach. The O^{2-} is considered in a sphere with radius $R = 2.668$ au and charge $+2$. This corresponds to a Madelung well depth $V_0 = 20.4$ eV [4], and $\epsilon_p(O(1)) \approx \epsilon_p(O(4))$. The Hartree–Fock calculation of O^{2-} in such a potential has given $\epsilon_p = -10.8$ eV.

Our main assumption is that the state of the electron trapped in the $O(1)^{2-}$ vacancy can be described as a superposition of an s-type function centred on the vacancy and of the totally symmetrical combination of the nearest neighbour oxygen p-orbitals. The ψ_s mentioned has been calculated as a solution of the Schrödinger equation with a rectangular potential well of depth V_0; for this $\epsilon_s = -9.92$ eV.

To calculate the F^+ ground state energy we use the standard Green's function method, having in mind that the excess charge $+1$ of the centre is strongly shielded by the large dielectric constant of the 123-system. To include the ψ_s in the consideration we proceed as in [1]. In an ideal crystal, additional ψ_s states are attributed to oxygens. Before the formation of the vacancy, these states are considered totally isolated from their surroundings. The formation of a vacancy introduces the coupling of ψ_s with the p-orbitals of neighbouring O^{2-} (the Cu^{2+} states are far in energy). At the same time the p-states of the missing oxygen are shifted to infinite energy. Now states can be found where the charge is redistributed in the defect region, which leads to the shifts in ϵ_s and ϵ_p. These two ($\Delta\epsilon_s$ and $\Delta\epsilon_p$) together with the sp-transfer integral t, act as perturbative parameters.

The defect region contains the $O(1)$ oxygen vacancy and the four neighbouring $O(4)$ ions. The unperturbed Green's function of A_g symmetry (group D_{2h}) contains two diagonal blocks:

$$G_s(E) = (E - \epsilon_s)^{-1}$$

$$G_A = \frac{a}{8\pi} \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} dk_x f(k_x, E) \frac{(1 - \cos(2k_x a))\langle pp\pi\rangle^2}{\langle pp\sigma\rangle^2 + \langle pp\pi\rangle^2 + 2\langle pp\sigma\rangle\langle pp\pi\rangle \cos k_x a} \quad (2)$$

where

$$f(k_x, E) = \frac{1}{E - \epsilon_1(k_x)} + \frac{1}{E - \epsilon_2(k_x)} + \frac{1}{E - \epsilon_3(k_x)}.$$

The perturbative matrix reads

$$W = \begin{pmatrix} \Delta\epsilon_s & 2t \\ 2t & \Delta\epsilon_p \end{pmatrix}. \quad (3)$$

The distorted states satisfy the equation

$$(\hat{G}\hat{W} - \hat{I})\hat{C} = 0 \quad (4)$$

where $\hat{C} = (C_v, C_p)$ and $C_v^2 + C_p^2 = 1$. The amount of the charge transferred from the vacancy to the neighbours is given by C_p^2. The solubility condition of (4) determines the localized state energy E_l as

$$\Delta\epsilon_s = E_l - \epsilon_s + 4t^2 G_A[G_A\Delta\epsilon_p - 1]^{-1}. \quad (5)$$

Approximating the excess and transferred charges as point entities, one estimates

$$\Delta\epsilon_s = \frac{\sqrt{2}e^2}{\epsilon_\infty a} C_p^2$$

$$\Delta\epsilon_s = -\frac{\sqrt{2}e^2}{\epsilon_\infty a} - \beta\Delta\epsilon_s \quad (6)$$

with $\beta = 0.521$ and $\epsilon_\infty = 5$. Substituting the expression for C_p from (4)

$$C_p^2 = \frac{4t^2 G_A^2}{4t^2 G_A^2 + (1 - G_a \Delta\epsilon_p)^2} \tag{7}$$

into (6) we arrive at the system of three equations (5) and (6) which determine E_l, $\Delta\epsilon_s$ and $\Delta\epsilon_p$ at a given t. We calculate the localized state energies as a function of t (see figure 1).
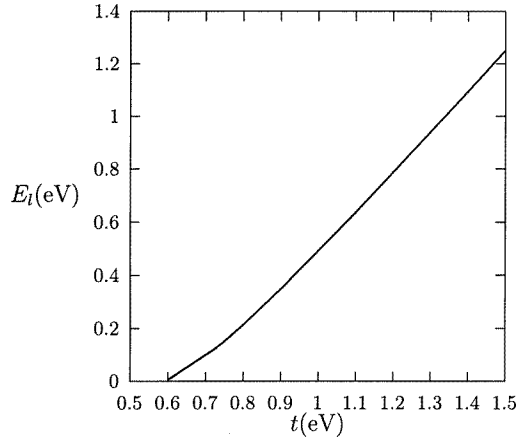

Figure 1. The energy of the localized vacancy level over the upper chain-band edge as a function of the sp-transfer integral.

The localized state appears beginning with the critical value of $t_c = 0.6$ eV being exceeded. It is larger than the value 0.35 eV found for the plane oxygen vacancy F^+ centre [1]. This hybridized (ψ_s, ψ_p) localized state is characterized by the essential concentration of the electronic charge inside the vacancy. For $t > t_c$ in a relatively wide interval, C_v^2 is of the order of 70% . Electronic correlations have not been directly taken into account in the present calculation. The localization of the majority of the charge inside of the vacancy is an advantage from the viewpoint of correlation effects. An account of them must not alter our conclusions at least qualitatively.

A rough estimate of t is 1 eV [3], then $E_l \approx 0.5$ eV. As a result, one can expect the localized energy level lying out of the chain band (also by 0.1 eV over the plane-oxygen band). This defect centre, as an electron trapped mainly in the chain O(1) vacancy of $YBa_2Cu_3O_{6+x}$ can be called the chain F^+ centre. At reasonable parameter values it must be stable. The formation of such chain F^+ centres has been supposed in the charge transfer mechanism of photoinduced conductivity effects in this material [2]. The present calculation serves as some support to the mechanism proposed in [2].

References

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