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Existence of a barrier between free and ferron-type (self-trapped) hole states in high-T_c cuprates

V. Hizhnyakov,* E. Sigmund, and G. Zavt*

Institut für Theoretische Physik, Universität Stuttgart, Pfaffenwaldring 57, 7000 Stuttgart 80, Federal Republic of Germany

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We study the behavior of an extra hole added to the ground state of the antiferromagnetically ordered CuO_2 plane. Both the Cu-O hybridization (characterized by parameter T) and the O-O transfer ($\sim t$) are taken into account, assuming $|T| > |t|$. As has been shown previously [V. Hizhnyakov and E. Sigmund, Physica C **156**, 655 (1988)], the energetically most favorable situation is given when a localized state is formed in which the antiferromagnetic order is locally destroyed and a small ferromagnetic cluster (ferron) is built up. We show that due to the increase of the magnetic energy induced by the spin-flip process ($E_s \sim 0.25$ eV) the localized and the metastable free-hole states are separated by a barrier of energy $\delta \sim E_s t/2T$, which can reveal itself in various kinetic phenomena.

I. INTRODUCTION

In a series of experimental works[1-3] it is demonstrated that the La and Y cuprates activated by Sr, Ba, and Ca dopants or by additional oxidation change their state from an insulating antiferromagnetically ordered phase to a normal or, below T_c, to a superconducting one. These transformations are caused by holes created by the doping or oxidation process. According to a model developed in Ref. 4 (see also Refs. 5–8), the holes introduced into the CuO_2 plane rearrange the antiferromagnetic (AF) order in their nearest vicinity to a ferromagnetic (F) one. Theoretical[4,9,10] estimations of the size of the ferromagnetically ordered cluster built up around a hole (so-called ferron[11]) give a number of 10–15 Cu^{2+} ions with parallel aligned spins. Within the Hubbard model in a strong-coupling limit the ferron binding energy is governed by Cu-O transfer integral[4] which is known to be ~ 1.5 eV. Since the transversal spin fluctuations are on a much smaller energy scale of exchange interaction $J \sim 0.1$ eV, the ferron states are expected to be stable against the spin fluctuations. The numerical diagonalization of t-J model[12] and its extension[13] also show evidences of the stability of short-range ferromagnetic order around the hole. A ferron itself is practically immobile, whereas inside the cluster the hole can move freely similar to a particle in a quantum well. The small geometrical size of the "well" leads to a size-caused quantization of the levels and to finite excitation energies. This, in a natural way, explains[14] the broad in-gap excitation band centered around 0.5 eV as observed in the infrared absorption spectra of weakly doped La and Y cuprates.[15] As a result of the ferron formation, when increasing the hole concentration and with it, the ferron concentration by doping, the clusters start to overlap and a (fractal) percolation network is built up. This leads to the destruction of the AF order and to the appearance of a metalliclike conductivity within the percolation network.[10] The local phase separation, described in Ref. 4, starting from the ferron picture, is also proposed and discussed in Ref. 16.

Besides the chemical doping or oxidation in pure La_2CuO_4 and $YBa_2Cu_3O_6$ (which are parent materials for high-T_c superconductors) the holes can be created via optical excitation across the insulating gap [1.6 eV (Ref. 15)]. Such transitions are known to correspond to the charge transfer from O^{2-} p orbitals to Cu^{2+} $d_{x^2-y^2}$ orbitals. Since the mobility of the extra electron in the Cu^{2+} sublattice with AF ordered spins is expected to be much lower than that of a hole in the nonmagnetic O^{2-} sublattice, the optically created electron and hole should separate and, at least for some time, exist independently. Within this time the holes tend to become self-trapped, forming ferron states. Indeed, the experimental investigations[17,18] of the photoinduced absorption in the materials under consideration display the induced broadband absorption centered around 0.5 eV with lifetime ~ 1 ms, which is attributed to the optical creation of localized in-gap excitations. This absorption band is analogous to the band observed for small chemical doping.[15,19] Since the photoinduced changes of the absorption coefficient in undoped materials resemble the absorption spectrum of doped (high-T_c) systems it is natural to assume that the localized species responsible for the photoinduced absorption are just the ferron hole states.

Concerning the self-trapping process, it is important to know if there is a barrier between the free-hole and ferron states. It is the main purpose of this present paper to show that the barrier indeed exists and to estimate its height. Such a barrier should lead to a remarkable temperature dependence of the free-hole–to–ferron relaxation process, which can manifest itself in various kinetic processes.

II. REDUCED HAMILTONIAN

We start from the AF ordered CuO_2 plane in the ground state ($|0\rangle$) of the system consisting of Cu^{2+} and O^{2-} ions only. In this state the $d_{x^2-y^2}$ band of Cu is half filled while all other d orbitals of Cu and the p orbitals of the O ions including the highest p_x, p_y band are totally filled. The ground state is separated from the first excited state by a rather wide charge-transfer energy gap of around 2 eV which is caused by the strong Coulomb repulsion (Hubbard energy U) of two electrons in the same $d_{x^2-y^2}$ Cu orbital. For large U, the ground state is practically completely polarized.

In the following, we are interested in the behavior of an independent extra hole added to the ground state $|0\rangle$ (e.g., by an optical excitation process followed by a separation of an electron-hole pair, as described above). In order to understand the dynamical processes the hole is involved in we consider two different situations.

(i) The hole with spin σ, which is created by removing an electron with spin $-\sigma$ from the AF ordered CuO_2 plane, moves in the AF ordered background; in the completely polarized situation the hole wave functions are projected only to the Cu spin orientation in $-\sigma$ direction. Therefore, the hole state can be described within so-called d^9L configuration consisting of Cu d function and a totally symmetric combination of p functions of four surrounding O ions (CuO_4 plaquette).

(ii) When turning one localized Cu spin from the manifold with $+\sigma$ spin direction, the Cu ion with turned spin disturbs the periodic sublattice containing $-\sigma$ Cu spins in which the hole [the same as in situation (i)] moves.

The behavior of the hole can be described by the effective Hamiltonian[20] (in the hole representation):

$$H = H_0 + H_T + H_t \,. \tag{1}$$

Here

$$H_0 = \varepsilon_d \sum_{m\sigma} \hat{n}^{(d)}_{m\sigma} + \varepsilon_p \sum_{m'\sigma} \hat{n}^{(p)}_{m'\sigma} \tag{2}$$

is the sum of one-particle Hamiltonian for $d_{x^2-y^2}$ and $p_{x,y}$ holes, ε_d and ε_p being the corresponding one-particle energies, $n^{(d)}_{m\sigma} = d^\dagger_{m\sigma} d_{m\sigma}$ and $n^{(p)}_{m'\sigma} = p_{m'\sigma} p^\dagger_{m'\sigma}$ the particle's number operators, and $d^\dagger_{m\sigma}$ and $p^\dagger_{m\sigma}$ are creation operators of particles in the copper (m) and oxygen (m') sites. Only oxygen p states, oriented along directions to the nearest-neighbor Cu ions, are taken into account;

$$H_T = T \sum_{(mm')} \sum_{\sigma} (d^\dagger_{m\sigma} p_{m'\sigma} + \text{H.c.}) \hat{n}^{(d)}_{m,-\sigma} \tag{3}$$

is the hybridization interaction between Cu $d_{x^2-y^2}$ and O $p_{x,y}$ states;

$$H_t = -t \sum_{(m'm'_1)} \sum_{\sigma} (p^\dagger_{m'\sigma} p_{m'_1\sigma} + \text{H.c.}) \tag{4}$$

is the oxygen-oxygen interaction. The sums in Eqs. (3) and (4) are assumed to be restricted to the nearest-neighbor Cu-O and O-O pairs, respectively; $t = (t_\sigma - t_\pi)/2 > 0$, where t_σ and t_π are usual p-p interaction integrals.

We neglect here the lower (hole) Hubbard level which is justified if $U \gg T$ and the difference of one-electron states $\varepsilon = \varepsilon^{el}_d - \varepsilon^{el}_p \ll U$. The relations between the parameters we use are $T \approx 1.5$ eV, $t_\sigma \gg t_\pi$, $t_\sigma \sim 2t \sim 0.4T$, and $\varepsilon \sim T$. For finite U the p-d charge fluctuations lead to an effective Cu-Cu interaction which produces the finite hole bandwidth of the order T^2/U. For $U \sim 10$ eV and values of other parameters given above, this width is considerably smaller than the width $4t$ caused by O-O transport. Therefore, we consider oxygen-oxygen interaction as the only interaction providing the hole transport.

In addition to the terms given in (1), the Hamiltonian of the system should include Cu-Cu and Cu-O spin-spin interactions as well.[21] However, what we will consider below is the hole wave packet of a large size of L in the AF ordered lattice with zero or one turned Cu spin. For such a particle, the latter interaction is weak and can be neglected (for large L the hole is mainly situated on oxygen ions in AF ordered area where the oxygen-hole–Cu spin-spin interaction vanishes). The Cu-Cu spin-spin interaction will be taken into account by adding the spin-flip energy E_s to the ferron energy.

Due to the exclusion principle for fermions in the statically AF ordered lattice the interaction H_T acts only within CuO_4 plaquette leading to a splitting of the hole states (described by Hamiltonian H_0) into five states with energies (see also Ref. 22)

$$E_1 = 0, \quad E_2 = E_3 = E_4 = \Omega - \varepsilon/2, \quad E_5 = 2\Omega \,, \tag{5}$$

where $\Omega = (4T^2 + \varepsilon^2/4)^{1/2}$ (the energy is counted from the lowest state). Since $T > t$, the separation of the lowest state from the other state ($\sim 2T$) considerably exceeds the widths of the band ($\sim t$) induced by the oxygen-oxygen transfer to which they couple. Therefore, the lowest state in the plaquette can be considered independently from the other states.

Taking only the lowest plaquette state E_1 and the O-O transfer into account, the particles in the lowest hole band can be described by the effective Hamiltonian[23]

$$h = -t_1 \sum_{(mm_1)} \sum_{\sigma} (c^\dagger_{m\sigma} c_{m_1\sigma} + \text{c.c.}) \,, \tag{6}$$

where

$$\begin{aligned} c^\dagger_{m\sigma} &= \sin\alpha\, d^\dagger_{m\sigma} + \cos\alpha\, P^\dagger_{m\sigma} \,, \\ P^\dagger_{m\sigma} &= \tfrac{1}{2} \sum_{(m')} p^\dagger_{m'\sigma} \,, \end{aligned} \tag{7}$$

with $t_1 = (t/2)\cos^2\alpha$, $\alpha = \arctan[4T/(\varepsilon + 2\Omega)]$, and (m') indicates the sum over oxygen ions which are nearest to the Cu ion at site m. For the assumed range of parameters ($|\varepsilon| \sim T$) one has $\alpha \approx \pi/4$, $t_1 \approx t/4$.

We consider now the energy of a hole wave packet in the two cases mentioned above: (i) in an ideal AF ordered CuO_2 lattice and (ii) in the same lattice but with one turned Cu spin.

III. FREE-HOLE STATES

For the ideally AF ordered lattice [case (i)] we choose the hole wave packet in the simplest exponential form

$$|\psi_L\rangle = A_L \sum_{m_x, m_y = 0}^{\infty} \exp[-(|m_x| + |m_y|)/2L] c^\dagger_{m_x m_y \sigma} |0\rangle \,, \tag{8}$$

where $A_L = 1/2L$, and m_x and m_y refer to the positions of the plaquettes in the x, y plane.

$$E^{(0)}_L = \langle \psi_L | h | \psi_L \rangle \approx -4t_1 + t_1/2L^2, \quad L \gg 1 \,. \tag{9}$$

As could be expected, the energy of a free hole is minimal when the size of the wave packet is large ($L \to \infty$).

IV. LOCALIZED-HOLE (FERRON) STATE

We take into account that turning a localized Cu spin disturbs the sublattice in which the hole moves [case (ii)]

and increases the magnetic energy by the amount $E_s \sim 0.25$ eV.[23] The localized ferron state is built up from the hole state of this localized "defect" Cu ion $|\psi_0\rangle = d^\dagger_{0\sigma}|0\rangle$ and from the totally symmetric combinations of the wave functions of four nearest-neighbor CuO_4 plaquettes. There are five such combinations, but only three of them listed below give a contribution to the ferron state:

$$|\psi_1\rangle = \tfrac{1}{2}\sum_{(m)} c^\dagger_{m\sigma}|0\rangle ,$$
$$|\psi_2\rangle = \frac{1}{2\sqrt{3}}\left(\sum_{(m)} P^\dagger_{m\sigma}|0\rangle - 4P^\dagger_{0\sigma}|0\rangle\right) , \tag{10}$$
$$|\psi_5\rangle = \tfrac{1}{2}\sum_{(m)} c^\dagger_{5m\sigma}|0\rangle ,$$

where

$$c^\dagger_{5m\sigma} = \cos\alpha\, d^\dagger_{m\sigma} - \sin\alpha\, P^\dagger_{m\sigma} ;$$

(m) indicates the sum over the nearest-neighbor copper ions situated around the central Cu ion (0) with turned spin. The state $|\psi_1\rangle$ and the combination

$$|\psi(0)\rangle = \sin\beta|\psi_0\rangle + \cos\beta|\psi_2\rangle \tag{11}$$

have the lowest energies $E_1 = 0$ and $E_0 = \Omega - (3T^2 + \varepsilon^2/4)^{1/2} \approx 0.27T$, respectively, with $\beta = \arctan[2\sqrt{3}T/(12T^2+\varepsilon^2)^{1/2}] \approx \pi/4$. Since all other states are separated by the distance $\sim 2t$ one may construct the ferron state from two latter states only:

$$|\psi^f_1\rangle \approx a_1|\psi(0)\rangle + (1-a_1^2)^{1/2}|\psi_1\rangle \tag{12}$$

($a_1 \approx 1\sqrt{2}$). For $t = 0$ the energy of this state given by

$$E^f_1 = E_S + \tfrac{1}{2}[E_0 - (4T^2\cos^2\alpha\sin^2\beta + E_0^2)^{1/2}]$$
$$\approx E_S - 0.4T \tag{13}$$

is very close to the exact value of the ferron binding energy $E^f = E_s(\sqrt{6}-2)T$ (for $\varepsilon = 0$).[4]

The ferron-type hole wave packet of large but finite size L can be introduced by the direct generalization of Eq. (12):

$$|\psi^f_L\rangle = a_L|\psi(0)\rangle + (1-a_L^2)^{1/2}|\psi_L\rangle . \tag{14}$$

The energy of this wave packet for $L \gg 1$ is equal to

$$E^f_L \approx E_S + a_L^2(E_0 + \tfrac{3}{2}t\cos^2\beta) + E_L^{(0)}$$
$$+ 2TA_L a_L \sin\alpha\sin\beta . \tag{15}$$

The small parameter a_L can be determined by minimizing this energy. Then one obtains

$$a_L \approx -\frac{T\sin\alpha\sin\beta}{L(2E_0 + 3t\cos^2\beta)} \tag{16}$$

and

$$E^f_L \approx E_S + E_L^{(0)} - \frac{T\sin^2\alpha\sin^2\beta}{2L^2(2E_0+3t\cos^2\beta)}$$
$$\approx E_S + E_L^{(0)} - \frac{T^2}{4L^2(1.1T+3t)} . \tag{17}$$

V. THE BARRIER

Comparing Eqs. (9) and (17) one observes that the free-hole state (with energy $E_\infty^{(0)} = -t$) is always energetically favorable for large-size wave packets ($L \to \infty$). However, if the condition $t < T^2/(1.1T+3t)$, i.e., $t < 0.42T$ is fulfilled the wave-packet energy *increases* with the rise of its size. This means that the localized wave packet, i.e., ferron state, possesses the lowest energy. The transition to the localized state occurs for a wave packet of size

$$L_B = \frac{T}{2[E_S(1.1T+3t)]^{1/2}} . \tag{18}$$

The energy at this point (with respect to $E_\infty^{(0)}$) representing the height of the barrier separating free- and ferron-hole states is

$$\delta_{ex} \sim \tfrac{1}{2}E_S[1.1(t/T) + 3(t/T)^2] . \tag{19}$$

This result is only slightly changed for a different Ansatz for the free-hole wave packet (8). For example, starting from a Gaussian wave packet for the free-hole state one gets a barrier height which is around 1.25 times lower than the one given in (19):

$$\delta_g \sim 0.4E_S[t/T + 3(t/T)^2] . \tag{20}$$

Expression (19) clearly displays the physics of the barrier: Suppose that the hole is created in the free (extended) state (what is usually the case for optical interband excitation). The free-hole state will not transform to the localized ferron state by first turning a Cu spin, since the latter process requires the large energy E_s. Instead, the hole state will be squeezed until the localization will provide the energy for turning a Cu spin and, hence, the final hole relaxation to the ferron state. The barrier is absent for $t = 0$ since in this case the particle is localized from the very beginning and the formation of ferron state leads to its partial *delocalization*.[4]

We want to emphasize that only the existence of a barrier leads to a metastable behavior of the free-hole states the lifetime of which can be rather large especially at low temperatures. In the above discussion we consider the transfer of a free hole to a ferron-type state with one turned spin. Depending on the parameters U, T, and ε, this small, localized ferron can further transfer to ferrons with more than five parallel Cu spins by successive turning of pairs of spins in the AF ordered lattice. For $U/T \sim 5$, $\varepsilon \sim T$, the energetically most favorable states are ferrons with 10–15 parallel Cu spins.[4]

Accepting the values of parameters mentioned above (i.e., $E_s \sim 0.25$ eV, $T \sim 1.5$ eV) and taking $t/T \sim 0.2$, one obtains the estimate $\delta \sim 20$–30 meV, $L_B \sim 1$. The barrier of such a height should remarkably influence the relaxation of the optically created free-hole state into the ferron-type state at low temperatures and should lead to a strong temperature dependence of this process. In experiment, the existence and the properties of the barrier can probably be deduced from the short-time kinetics of the photoinduced mid-ir absorption in pure La_2CuO_4 and $YBa_2Cu_3O_6$.

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*Permanent address: Institute of Physics, Estonian Academy of Sciences, Riia 142, Tartu, Estonia.

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