Localized magnetic centers in the compound $YBa_2Cu_3O_{6+x}$ ($x \ll 1$)

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A model is proposed for the electronic processes which occur as the basal planes in a 1-2-3 high-T_c compound become filled with oxygen. An ionic structure is proposed for these planes. Localized magnetic moments form in the insulating phase of this compound. They exhibit a paramagnetic behavior, without an ESR signal.

As the oxygen content in the compound $YBa_2Cu_3O_{6+x}$ ($0 < x < 1$) is varied, the basal plane is known to become filled with vacancies [in O(1) or O(5) sites[1]]. At $x \approx 0.5$, CuO chains form, and the system undergoes a transition to a metallic (and superconducting) state. Since we do not yet have a good theoretical understanding of the insulator-metal transition or of the nature of the metallic phase in this compound, it seems worthwhile to attempt to approach this transition from the insulator side, working from the electronic (ionic) structure of $YBa_2Cu_3O_6$ (i.e., the compound with $x = 0$). This structure is understood and is generally accepted. For example, a scheme for the electronic processes which accompany the filling of the basal plane with oxygen was recently proposed in Ref. 2. Emery's model was used there to examine the chains which form in this plane and which consist of Cu^{2+}, O^- (spin-1/2), and O^{2-} (spin-0) ions, with an antiferromagnetic exchange $J \approx 10^3$ K between neighboring spins. The total number of neighboring spins is even, since each oxygen furnishes two spins to the initially spinless basal plane. It follows in particular from this picture that at small values $x \ll 0.5$ (in the insulating phase), at which chains with few oxygen atoms are predominant if the distribution is random, the chains would be completely inert from the magnetic standpoint (the singlet ground state would be separated from the excited states by a gap $\sim J$). These chains would not make a contribution up to terms on the order of x^4 in either the static susceptibility χ or the ESR signal.

In this letter we wish to propose a slightly different electronic structure for localized centers, associated with oxygen atoms which have penetrated into the basal plane. As we will see below, such centers should have some characteristic magnetic properties. These properties might be of assistance in an experimental test of whether such centers can exist. If they are confirmed to exist, then taking them into account may also prove important in a subsequent derivation of a theory for the transition of this system to a metallic state.

We do not yet have a clear picture of the distribution of oxygen which has penetrated into the basal plane with respect to the number (n_O) of oxygen atoms in a cluster. Under the assumption of a random distribution, the overwhelming majority of

the atoms which have entered should form isolated centers (with a relative probability $w_1 \sim x$), while the others should form clusters of two, three, etc., atoms in neighboring sites. The probabilities for the formation of these clusters fall off as $w_2 \sim x^2$, $w_3 \sim x^3$, ... If, on the other hand, some correlation promotes the formation of long chains,[3] then one might be led to believe that again in this case, at $x \ll 0.5$, a significant amount of the oxygen which has entered the compound would belong to fragments of short length, although the probabilities for such fragments, w_{n_O}, would no longer be given by these simple power-law relationships.

As in Ref. 2, the simplest center which arises near an isolated oxygen atom has an obvious structure, which is the only one possible: A neutral O atom is ionized to the O^{2-} state. The two nearest copper ions go from the Cu^+ state to the Cu^{2+} state. The result is the formation of a Cu^{2+}–O^{2-}–Cu^{2+} dumbbell center (Fig. 1a), with a singlet ground state and a triplet excited state. Consequently, there is actually no contribution $\sim w_1$ to the magnetic properties of the system at low temperatures, $T \ll T_N \ll J$. We restrict the entire discussion below to such temperatures. However, we would like to point out that, through the exchange interaction J' with the neighboring, magnetically ordered CuO_2 planes, a dumbbell center creates an effective interplanar ferromagnetic coupling $\propto (J')^2/J$. This coupling frustrates the weak antiferromagnetism of the interplanar coupling in the original crystal and may thus influence the stability of the long-range magnetic order.

The distinction between this approach and that of Ref. 2 can be seen even when we consider a cluster of only two oxygen atoms. According to Ref. 2, a Cu^{2+}–O^{2-}–Cu^{2+}–O^-–Cu^{2+} chain (the L configuration) should arise in this case. More favorable from the energy standpoint, however, is a process in which an additional hole undergoes a transition from an O^- ion to one of the nearest Cu^+ ions which do not

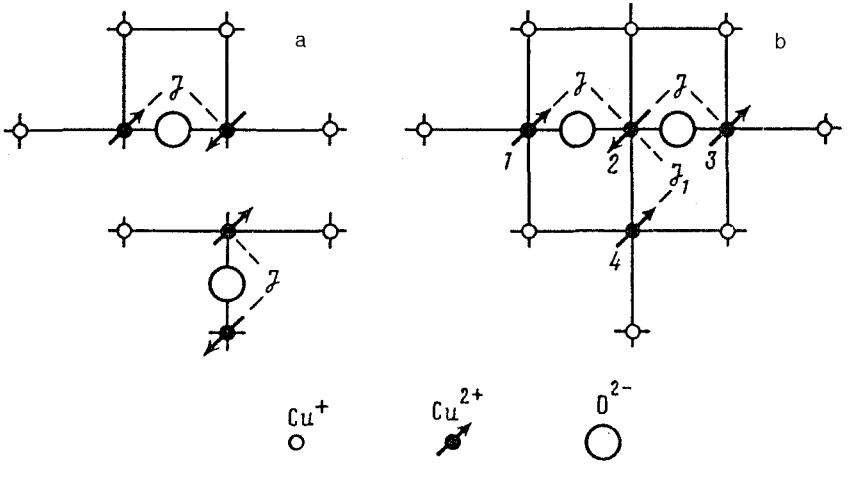

FIG. 1. Localized magnetic clusters in the basal plane of the 1-2-3 compound. a—Geometrically different dumbbell centers; b—T center.

belong to this linear cluster. In fact, the difference between the total electronic energies of the $Cu(3d^{10})$–$O(2p^5)$ and $Cu(3d^9)$–$O(2p^6)$ configurations for a pair of nearest-neighbor ions is about 5 eV, according to Ref. 4. Furthermore, despite some possible decrease in the latter value because of the greater length of the corresponding Cu–O bond, one might suggest that such an estimate is a sufficient basis in principle for adopting the hypothesis that the existence of O^- ions in the compound $YBa_2Cu_3O_{6+x}$ is unfavorable in the region of its insulating phase. It is not difficult to see that among the several permissible geometric configurations of these clusters (without O^-), the formation of a T-shaped center,[1)] as shown in Fig. 1b, is preferable from the standpoint of the interionic Coulomb energy of these clusters. Its magnetic structure is determined by the Cu^{2+} ions and consists of a triad $(\vec{S}_1, \vec{S}_2, \vec{S}_3)$ of spins with strong antiferromagnetic couplings and a weakly bound spin $\vec{S}_4$. The value of the interaction J_1 of the latter with $\vec{S}_2$ is determined by a competition between the direct ferromagnetic exchange and the indirect antiferromagnetic exchange. In general, it may be of either sign.

The energy spectrum for this spin Hamiltonian

$$\mathcal{H}_T = J\vec{S}_2(\vec{S}_1 + \vec{S}_3) + J_1\vec{S}_2\vec{S}_4 \qquad (|J_1| \ll J) \tag{1}$$

of an isolated T center can be calculated very simply. For example, in the case $J_1 > 0$, which is the case of most physical interest, the low-energy part of this spectrum consists of a triplet gound state with $E_{tr} = 0$ (which corresponds to a total spin $S = 1$ of the center) and a singlet ($S = 0$) level with $E_{sg} = J_1$. The symmetric position of the T center with respect to the magnetic sublattices of the antiferromagnetic matrix (the CuO_2 planes) means that we can classify this center as a "quadrupole impurity center."[5] The properties of centers of this type differ substantially from those of ordinary paramagnetic centers, despite the fact that the mean exchange field vanishes at a center. According to Ref. 5 (see also the review in Ref. 6), incorporating the interaction of the spin of a quadrupole center with virtual magnons of the antiferromagnetic matrix gives rise to the following effective Hamiltonian in second-order perturbation theory in the parameter J' (in the case at hand, a relatively weak exchange interaction with those Cu^{2+} spins of magnetically ordered CuO_2 planes which are closest to the T center):

$$\mathcal{H}_{qdr} = DS_z^2, \quad D \sim (J')^2/J \ . \tag{2}$$

Here the z axis is along the antiferromagnetic vector of the matrix. With $S = 1$, we obviously find a splitting of the triplet level into two parts in (2): a singlet ground level ($S_z = 0$) and a doublet level ($S_z = \pm 1$) with an energy D. This level structure can be used to describe the splitting of the E_{tr} term of a T center in the case $D \ll J_1$. Here the position of the E_{sg} level remains unchanged (Fig. 2a). One consequence of the splitting should be that a T center has no ESR signal with a linear dependence of the frequency on the external magnetic field. This conclusion agrees with numerous experimental observations.[7] On the other hand, the T centers still have a magnetic "activity," making a contribution proportional to w_2 to the magnetic susceptibility of the system. At $T \ll J_1$, this contribution is given by

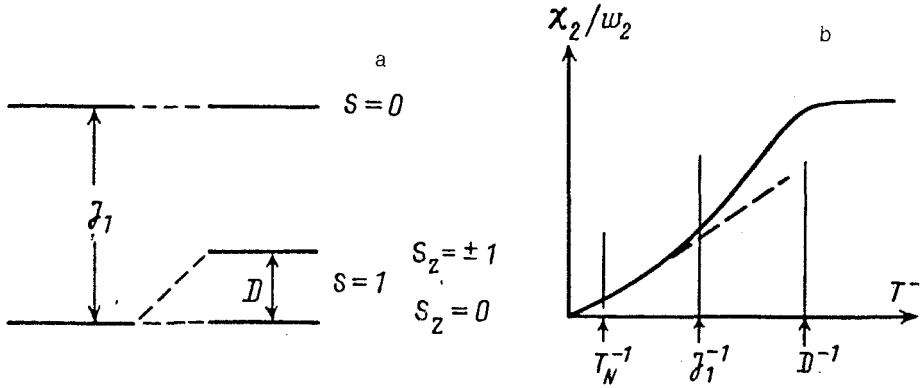

FIG. 2. a—Positions of the lowest spin levels with and without consideration of the operator $\mathscr{H}_{qdr}$; b—temperature dependence of the magnetic susceptibility of a T center.

$$\chi_2 \approx \frac{2w_2}{D}\frac{1-e^{-D/T}}{1+2e^{-D/T}} \approx \begin{cases} \frac{2w_2}{D}(1-3e^{-D/T}), & T \ll D; \\ \frac{2w_2}{3T}, & D \ll T \ll J_1 \end{cases} . \tag{3}$$

At $J_1 \ll T \ll T_N$, the filling of the E_{sg} singlet level results in a replacement of the factor of 2/3 by a factor of 1/2 in the paramagnetic susceptibility (Fig. 2b). We should stress that the contribution of the spin of an individual T center to the low-temperature susceptibility is larger than that of the spin of the matrix by an extremely large factor, $\sim J/D \gg 1$.

In the case $D \gg J_1$, the latter quantity can be ignored. In this case the interaction of (on the one hand) the spin $\vec{S}_4$ and the total spin of the triad $\vec{S}_{123} = \vec{S}_1 + \vec{S}_2 + \vec{S}_3$, which is also equal to 1/2 in the ground state, with (on the other) the antiferromagnetic CuO_2 planes gives rise to an effective interaction between $\vec{S}_4$ and $\vec{S}_{123}$. This interaction is decribed by the Hamiltonian [cf. (2)].

$$\mathscr{H}_{eff} = -D'(S^x_{123}S^x_4 + S^y_{123}S^y_4), \quad D' \sim D. \tag{4}$$

The spectrum of operator (4) consists of an $S=0$ ground singlet, a doublet ($S=1$, $S_z = \pm 1$) with an energy D', and a singlet ($S=1$, $S_z=0$) with an energy $2D'$ (Ref. 8). Here, as in the case described above, there is no ordinary ESR signal, and the temperature dependence of the susceptibility is given by

$$\chi_2 \approx \frac{2w_2}{D'}\frac{1-2e^{-D'/T}}{1+2e^{-D'/T}+e^{-2D'/T}} \approx \begin{cases} \frac{2w_2}{D'}(1-2e^{-D'/T}), & T \ll D'; \\ \frac{w_2}{T}, & T \gg D' \end{cases} . \tag{5}$$

We see that this result is qualitatively the same as (3) in the low-temperature region, but there is no change in the numerical factor in its paramagnetic part.

Finally, we note that if the interaction J_1 in Hamiltonian (1) has the ferromagnetic sign (<0), the ground level of the T center is a singlet with $E_{sg}=0$, and the excited state is a triplet with $E_{tr} = |J_1|$. If $D \ll |J_1|$, the T dependence of the susceptibil-

ity χ_2 has a Schottky maximum at $T \approx 1.6|J_1|$, and the paramagnetic behavior is determined by $\chi_2 \approx w_2(2T)^{-1}$. If, on the other hand, we have $D \gg |J_1|$, then we of course will have essentially the same situation as is described by expressions (5).

A similar analysis for chains with a larger value of n_O, in which all the oxygen ions are divalent, shows that such clusters will contain spins with a nearly paramagnetic behavior, regardless of n_O. The reasons lies in the presence of Cu^{2+} ions, outside the main chain. In the case of L centers, the even parity of the total number of antiferromagnetically coupled spins belonging to these centers, as mentioned above, should keep these centers from contributing to the low-temperature magnetic susceptibility of the system.

In summary, according to the arguments presented here, the system $YBa_2Cu_3O_{6+x}$ in its insulating state should exhibit a paramagnetic increase in susceptibility at low temperatures, withou an ESR signal (in fields which are not too strong). Furthermore, all clusters will, like dumbbells, have a frustrating effect on antiferromagnetic interplanar couplings, although this effect does not rule out the existence of other mechanisms which would disrupt the long-range magnetic order in the 1-2-3 compounds (in particular, the mechanisms discussed in Refs. 9–11). In general, these other mechanisms still await corresponding experimental and theoretical research.

[1)]Here we might add that, "from the standpoint" of the internal interionic energy, a T center is stabler than an L center by ≈ 14 eV. There is, on the other hand, a disadvantage, because of the ionization potential, primarily that of the Cu^+ ion. If we use the vacuum value of this potential, ≈ 20 eV, as an estimate, we find that the L center is preferable. If the role of the Cu^+ ionization potential in the 1-2-3 compound is instead estimated from the distance (a few electron volts) to the copper s conduction band, then the formation of a T center clearly becomes more favorable. As we have already mentioned, we will be assuming the latter below, although actually the energies of these centers are probably fairly close together.

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