Magnetic short-range order in CuO_2 planes of high-T_c superconductors

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The electronic and magnetic structure at the CuO_2 planes of high-T_c oxides as a function of hole doping is analyzed. The Emery model is solved in a mean-field approximation that includes spin correlations between copper atoms. It is found that the long-range antiferromagnetic order is destroyed with 0.025 extra holes per unit cell, while the magnetic moments of Cu are slightly reduced in the disordered phase. The antiferromagnetic long-range order is lost by the presence of ferromagnetic Cu—Cu bonds with the bridging oxygen atoms antiferromagnetically aligned with respect to them. For doping doses corresponding to the superconducting phase, the short-range antiferromagnetic correlations between Cu atoms are not completely lost, as is the case experimentally.

It is well known[1,2] that high-T_c oxides are antiferromagnetic (AF) insulators for their undoped reference compounds like La_2CuO_4 and $YBa_2Cu_3O_6$. The AF long-range order is lost upon doping, the material becoming superconducting. It is also well established experimentally that the magnetic moment of Cu atoms is not lost for doping doses corresponding to the superconducting phase, and even some antiferromagnetic (AF) correlation is kept in this phase.[3,4] From the theoretical point of view there have been several approaches to study the effects of extra holes in the AF ground state. Among them we mention (i) studies of finite clusters of atoms in mean-field approximations,[5-7] (ii) mean-field calculations in infinite systems where the electronic correlations are somehow included,[8-11] and (iii) study of highly correlated systems in small clusters of atoms.[12-15] Although these calculations have helped us to understand the effect of extra holes, there is not a unified picture to explain the rapid decreasing of the AF correlation length with doping and the magnetic ordering of the ground state after the AF long-range order is lost.

In this work we develop a model which accounts for the rapid disappearance of the long-range AF order with doping and gives rise to a new ground state. The emphasis is put in treating the electronic correlations and the disorder induced by the extra holes on the same footing. To study the electronic and magnetic structure of the CuO_2 planes we consider the well-known two-band Hamiltonian[16]

$$H=\sum_{i,\sigma}E_i n_{i\sigma}+\sum_{\langle i,j\rangle,\sigma}t_{ij}c^{\dagger}_{i\sigma}c_{j\sigma}+\sum_i U_i n_{i\uparrow}n_{i\downarrow}\ , \tag{1}$$

where the index i (j) runs over the sites of the CuO_2 planes. The parameters $E_i=E_p, E_d$ and $U_i=U_p, U_d$ are the orbital energies and intra-atomic Coulomb repulsion for the O p_σ orbitals and Cu $d_{x^2-y^2}$ orbitals, respectively. The hopping matrix element of p-d orbitals is represented by t_{ij}. We simplify the above Hamiltonian by considering the mean-field decoupling

$$n_{i\uparrow}n_{i\downarrow}\cong\langle n_{i\uparrow}\rangle n_{i\downarrow}+\langle n_{i\downarrow}\rangle n_{i\uparrow}-\langle n_{i\uparrow}\rangle\langle n_{i\downarrow}\rangle\ , \tag{2}$$

such that no possible spin canting is allowed. So, we exclude the quantum spin fluctuations from the beginning. To solve the problem, as is stated, we consider an alloy analogy similar to the one developed to study the disappearance of ferromagnetism with temperature in transition metals.[17,18]

We distinguish two kinds of Cu atoms with magnetic moment either up ("+") or down ("−") and in each Cu atom the electrons can indeed have spin up or down. The magnetic moment is then defined as

$$\mu_i=\langle n_{i\uparrow}\rangle-\langle n_{i\downarrow}\rangle\ . \tag{3}$$

The oxygen atoms can also have spin polarization and can be classified according to moment orientation of their nearest-neighbor Cu atoms. We have therefore O^{++}, O^{--}, and O^{+-} atoms.

In order to calculate the electronic structure of this system we consider the method developed by Verges and coworkers for alloys.[19-22] We define the short-range magnetic order between nearest-neighbor Cu atoms by a single parameter p in the following way: Consider one particular Cu atom with a magnetic moment, if $p=0$ the magnetic moment of its nearest-neighbor Cu atom is antiparallel (AF correlation) and for $p=1$ it is parallel (ferromagnetic correlation). Any intermediate value of p would describe a nonordered situation. In particular, $p=\frac{1}{2}$ is a completely disordered system. We can write down the following equations for the self-energies of the different Cu atoms (see Fig. 1):

$$\begin{aligned}G^{+}_{ii\sigma}(E)&=(E-E_d-U_d\langle n^{+}_{d\bar\sigma}\rangle-4\Sigma^{+}_{\sigma})^{-1}\\&=p\left(E-E_d-U_d\langle n^{+}_{d\bar\sigma}\rangle-t^{\sigma}_{\rm eff}(+,+)-3\Sigma^{+}_{\sigma}-\frac{[t^{\sigma}_{\rm eff}(+,+)]^2}{E-E_d-U_d\langle n^{+}_{d\bar\sigma}\rangle-t^{\sigma}_{\rm eff}(+,+)-3\Sigma^{+}_{\sigma}}\right)^{-1}\\&\quad+(1-p)\left(E-E_d-U_d\langle n^{+}_{d\bar\sigma}\rangle-t^{\sigma}_{\rm eff}(+,-)-3\Sigma^{+}_{\sigma}-\frac{[t^{\sigma}_{\rm eff}(+,-)]^2}{E-E_d-U_d\langle n^{+}_{d\bar\sigma}\rangle-t^{\sigma}_{\rm eff}(+,-)-3\Sigma^{-}_{\sigma}}\right)^{-1}\ ,\end{aligned} \tag{4}$$

and a similar equation for "down" Cu atoms, where $t^{\sigma}_{\rm eff}(\pm,\pm) = t^2_{pd}(E - E_p - U_p \langle n^{\pm,\pm}_{p\bar{\sigma}} \rangle)^{-1}$, with $\langle n^{\pm,\pm}_{p\bar{\sigma}} \rangle$ the occupation number of the $O^{\pm,\pm}$ atom. These equations can be solved to obtain the different local Green's functions and from them the mean occupation numbers

$$\langle n_{i\sigma} \rangle = -\frac{1}{\pi} \int_{-\infty}^{E_F} \mathrm{Im} G_{ii\sigma}(E)\, dE \ . \tag{5}$$

For a given set of Hamiltonian parameters, a given hole concentration and a given value of p Eqs. (4) and (5) can be solved self-consistently to obtain the equilibrium electronic configuration. In our calculation we do not impose any symmetry constraint to the different occupation numbers. The ground state can be paramagnetic, ferromagnetic, antiferromagnetic, ferrimagnetic, charge-density wave, or any combination of them. The total electronic energy can also easily be obtained to identify the value of p which gives the minimal energy and then the corresponding short-range magnetic order at each hole concentration.

In Fig. 2 we show the results for the total electronic energy versus the parameter p for various hole concentrations. Also in the figure the resulting short-range magnetic ordering is indicated. The Hamiltonian parameters are those proposed by Tjeng, Eskes, and Sawatzky,[23] namely $t_{pd} = 1.47$ eV, $U_d = 9.7$ eV, $U_p = 5.7$ eV, and $E_p - E_d = 2.5$ eV. Calculations for other available sets of parameters yield similar results. There are several points worth noticing in the figure: (i) Antiferromagnetism is lost for small hole concentrations (see below for details). (ii) When antiferromagnetism is lost the new phase contains a fraction of the Cu—Cu bonds with parallel orientation (although the number of up and down moments is the same and the system is paramagnetic). In these bonds the shared O atom develops a small antiparallel magnetic moment. This is in accordance with the views of Aharony *et al.*,[24] and also found in exact small-cluster solutions.[13] (iii) As the number of holes increases the fraction of antiferromagnetic Cu—Cu bonds decreases. (iv) When increasing the number of holes the total energy curves become shallower, indicating a mixing of a large number of magnetic configurations with a large fluctuation of the oxygen magnetic moment amplitude. (v) The magnetic moment of Cu does not disappear with the antiferromagnetic long-range order.

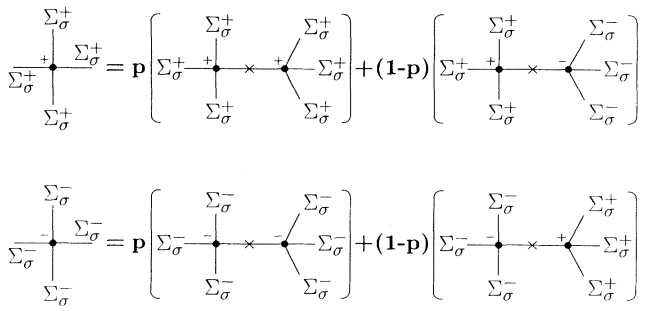

FIG. 1. Relation between the self-energies appearing in Eq. (4), for Cu^+ and Cu^- atoms.

In order to show how the different occupations and magnetic moments vary with the hole concentration we have plotted them in Figs. 3(a) and 3(b), respectively, for the doping values shown in Fig. 2 and at the equilibrium magnetic configurations. We observe that the magnetic moment of Cu decreases monotonically with the increase of the hole concentration, whereas the magnetic moment of the oxygen atoms between ferromagnetically correlated Cu atoms increases with the holes content. From the figure we also see that the added holes occupy both Cu and O atoms, being more located at the O^{++} (O^{--}) atoms.

To see in more detail the breaking of the AF long-range order by the presence of holes, we show in Fig. 4 the variation of the staggered magnetization and the order parameter p *at equilibrium* with the hole concentration. We observe that for a hole concentration of 0.025 per unit cell the antiferromagnetic ordering ($p = 0$) is lost. (However, the possibility of other kinds of magnetic order, in particular, spiral or domain walls, cannot be excluded from our calculations). The transition from AF to the magnetically disordered phase takes place at a very narrow doping range, but whether or not the transition is abrupt cannot be assessed from the calculation due to numerical uncertainties. In Fig. 4 we also show (with a dashed line) how the AF magnetic order disappears when the constraint of no ferromagnetic Cu—Cu bonds is imposed to the system. In this case the AF order is lost by the disappearance of the Cu magnetic moments. The paramagnetic phase P of our model, however, is a nonmagnetic phase with nonzero magnetic moments.

Finally, in Fig. 5 we have plotted the total densities of states for the equilibrium atomic configurations obtained in Fig. 2. We first observe the antiferromagnetic

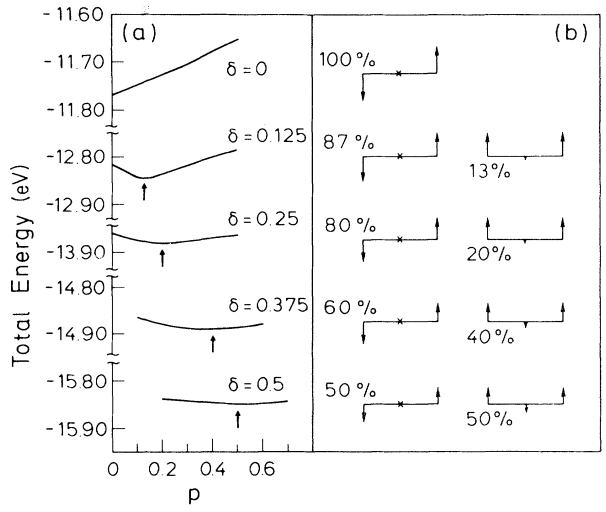

FIG. 2. (a) Total energy vs the short-range order parameter p for various doping concentrations. (b) Magnetic moment configuration at equilibrium.

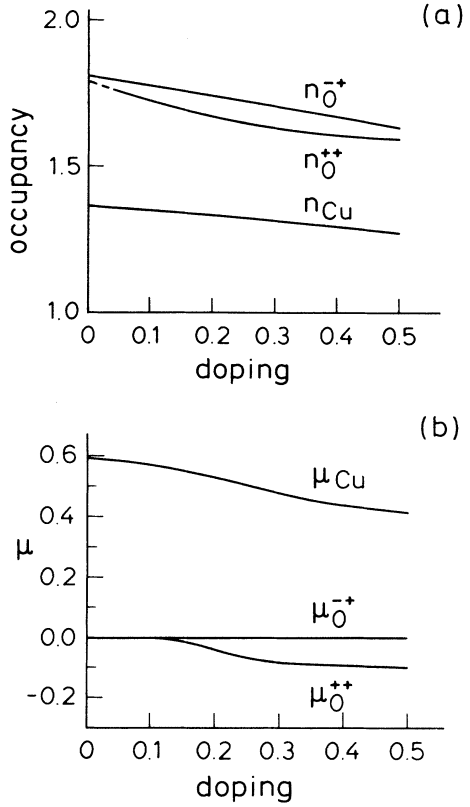

FIG. 3. Variation of the electronic distribution with doping at different atoms: (a) occupation numbers, (b) magnetic moments (in Bohr magnetons).

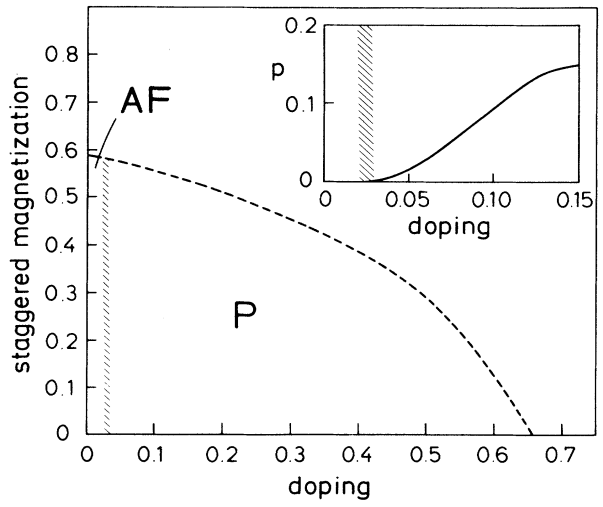

FIG. 4. Staggered magnetization vs doping. The phase P corresponds to a paramagnetic phase produced by the disordered orientation of the atomic magnetic moments. The dashed line represents the results when only AF ordering of the Cu atoms is allowed. Inset: variation of the short-range order parameter p vs doping near the AF-P transition. The hatched regions indicate uncertainty in the numerical solutions.

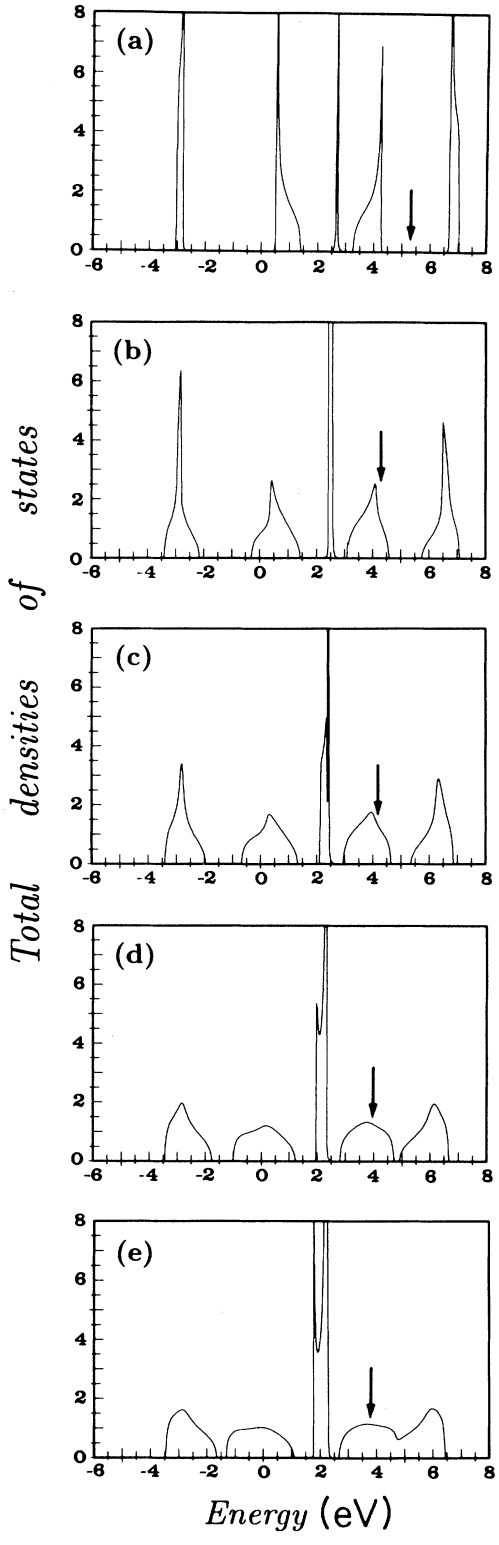

FIG. 5. Total densities of states for the equilibrium configurations corresponding to the dopings of Fig. 2. Panels (a), (b), (c), (d), and (e) stand for $\delta = 0$, 0.125, 0.25, 0.375, and 0.5, respectively. The arrows indicate the position of the Fermi level.

gap at the Fermi level in the absence of doping. The excitation gap is approximately 2.4 eV, in agreement with experiments.[25] See also Ref. 5. (When the local-density-approximation parameters[26] are used the gap increases by 40%). This result is consistent with the assumption that these systems are charge-transfer insulators. Now, when holes are included there are localized states near the AF gap edges, which in our uniform calculation develop a band that closes the gap for very high hole concentrations. For small doping the Fermi level lies at this band, whose states are mainly weighted at the O^{++} (O^{--}) atoms, as analysis of the local densities of states reveals. We observe too from the sequence of pictures in Fig. 5, a possible mechanism for the pinning of the Fermi level with doping. Also seen is the shifting and broadening of the nonbonding oxygen band, which is due in this case to the appearance of a small magnetic moment at oxygen sites.

The results of our calculation can be summarized as follows: (i) AF long-range order disappears with a small hole concentration in a process similar to the one proposed by Aharony *et al.*[24] (ii) The magnetic moment of Cu when there are no extra holes is $0.59\mu_B$, in agreement with experiments which range from $0.4\mu_B$ in La_2CuO_4 (Ref. 27) to $0.64\mu_B$ in $YBa_2Cu_3O_6$ (Ref. 28). (iii) The magnetic moment of Cu does not disappear in the superconducting phase in agreement with experiments. This is plausible because the magnetic energies involved are much higher than the pairing energies. (iv) In the superconducting doping region there is still some antiferromagnetic correlation, since the pair correlation parameter p ranges $0 < p < 0.5$ in this doping range. (v) The AF coupling between Cu and O when Cu-Cu ordering is ferromagnetic makes the Cu atoms be surrounded by antiparallel O atoms. The clustering of such bonds, forming local singlets, is expected to reduce the total energy. (vi) Only uniform systems are considered in the calculations. Domain lines,[5] vortices, and other local configurations cannot be accounted for in our calculation. In the same way, no possible spin canting has been considered. This means that the itinerant results presented here are strictly valid for classical spins, nevertheless we stress the concordance with the experimental situation.

So far, we have solved the two-band Emery model in an unrestricted mean-field Hartree-Fock-like approximation, including an extra degree of freedom to take into account the static disorder induced by holes, and found that the magnetic order is lost very rapidly. Whether this picture will persist when the dynamical disorder produced by the quantum spin fluctuations is considered is still an open question. Improvement of the calculations along these directions is in progress.

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