Importance of Local Band Effects for Ferromagnetism in Hole-Doped La_2CuO_4 Cuprate Superconductors

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Band calculations for supercells of $La_{(2-x)}Ba_xCuO_4$ show that the rigid band model for doping is less adequate than what is commonly assumed. In particular, weak ferromagnetism can appear locally around clusters of high Ba concentration. The clustering is important at large dilution, and averaged models for magnetism, such as the virtual crystal approximation, are unable to stabilize magnetic moments. These results give support to the idea that weak ferromagnetism can be the cause of the destruction of superconductivity at high hole doping.

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The fascinating phase diagram of the cuprate high temperature superconductors still remains a great mystery in the field of condensed-matter physics [1]. Antiferromagnetic (AFM) spin fluctuations are probably also relevant to the properties of the doped metallic state because they mix with phonons [2,3] and they provide mechanisms able to boost the electron-phonon interaction [4]. While many investigations have focused on underdoped phases [5,6], little attention has been devoted to the overdoped regime, where the abrupt suppression of superconductivity for a critical doping cannot be easily understood in term of the standard BCS theory. Only recently, Kopp, Ghosal, and Chakravarty [7] have suggested that ferromagnetic (FM) fluctuations compete with superconductivity in the overdoped regime. These authors have considered an itinerant picture and have used it to justify the rich phenomenology of the overdoped cuprates. In particular, the termination of the superconductivity in the overdoped regime could mark a quantum critical point beyond which there should be a FM phase at zero temperature. A FM ground state excludes a s or d wave superconductivity of the singlet variety [7]. The electron-phonon coupling, which may contribute to superconductivity, is also inhibited by FM spin fluctuations [8,9].

Electronic structure calculations performed by Perry, Tahir-Kheli, and Goddard [10] using the spin unrestricted Becke-3-Lee-Yang-Parr (B3LYP) hybrid functional successfully produced a 2.0 eV band gap and antiferromagnetism in (undoped) La_2CuO_4. However, Paier, Marsman, and Kresse [11] have raised serious concerns on the suitability of the B3LYP potential in metallic phases, and subsequent B3LYP calculations for minimal size supercells of $La_{2-x}Sr_xCuO_4$, corresponding to $x = 0.125$, 0.25, and 0.5 [12], have predicted FM solutions. This in contrast to the nonmagnetic or AFM fluctuating states found in real, weakly doped systems. On the other hand, band calculations based on the local spin-density approximation (LSDA) yield the correct Fermi surface and a reasonable band dispersion [13], and electronic structure studies on manganites [14] have shown that the LSDA provides a reliable potential for predicting both metallic and ferromagnetic phases. The difficulty with the LSDA is rather to describe correctly the AFM, insulating state of the undoped cuprates, but one should note that LSDA calculations for high-T_c cuprates with *off-center* linearization energies describe well both the undoped and the doped counterparts [15]. This fact indicates that two very different ground states are almost degenerate and that only small LSDA corrections are needed to bring the two states into the correct order [16].

In this Letter, we confirm that the LSDA electronic structure of $La_{2-x}Ba_xCuO_4$ in the overdoped regime is consistent with weak ferromagnetism appearing locally around clusters of high Ba concentration. Our results from first principles validate the hypothesis by Kopp, Ghosal, and Chakravarty [7] that FM order and superconductivity are competing in overdoped samples.

Our band calculations are performed with the linear muffin-tin orbital (LMTO) method [17–19] for supercells with 2 or 16 formula units (f.u.) of La_2CuO_4. The elementary 7-site unit cell is doubled along the $\hat{x}$ direction in the former case, which yields a (2, 1, 1) extension of the elementary cell. The cell is then doubled along the 3 directions in the case of the large cell, leading to a (4, 2, 2)-extended cell with 112 atomic sites totally. The supercells in Ref. [12] were adjusted to optimal size for each doping x, while here the use of a larger supercell of identical dimension for different x allows for some randomness in the local order. The basis set includes ℓ up through 3 for La and Cu sites and up through 2 for O sites [20]. The number of k points is 84 in the calculations for the small cell, and it varies from 4 to 125 in 1/4 of the Brillouin zone for the large cell. All sites in the cell are considered as nonequivalent throughout the self-consistent calculations. Other details of the methods can be found elsewhere [17–19,21,22].

Our result for paramagnetic La_2CuO_4 is in excellent agreement with the full potential calculation by Yu,

Freeman, and Xu [23]. As was mentioned above, doped La_2CuO_4 is metallic, LSDA calculations describe its band dispersion and Fermi surface adequately, and AFM can be promoted by use of offset linearization energies in LMTO. The present calculations are based on a normal choice of linearization energies, and therefore we expect an underestimation of the tendency towards magnetism, even in the doped cases.

The magnetic moments for the three possible configurations for $x = 1$ in the supercells with 2 f.u. (14-site cells) are shown in Table I. Small but stable magnetic moments develop in the two configurations where the two Ba atoms in the cell belong to the same plane (i.e., are situated next to each other along $\hat{x}$ and $\hat{y}$) or when they are shared between two planes. The two Cu in both configurations have almost equal magnetic moments and equal local density of states (DOS) at the Fermi energy E_F. Planar oxygen atoms have small magnetic moments, but the apical oxygen atoms between La/Ba and Cu have almost as large a magnetic moment as Cu. Oxygen magnetism is somewhat unusual, but there are cases reported in the literature like for a half-metallic Rb_4O_6 [24]. This participation of the apical O to the spontaneous magnetic polarization cannot be understood from the Stoner model because there is no clear correlation between local DOS at the apical O and the magnetic moment. Therefore, other mechanisms such as charge transfers and hybridization with neighbors are vital to explain the magnetization of the apical O atom [12]. In our case, the charges on the apical O atoms are somewhat larger when these O sites are between the Cu atom and the Ba atom rather than between the Cu atom and the La atom, while the magnetic moments are largest on the O atom close to the La plane when the La/Ba atoms are fully occupying a plane. This trend is reversed when there is alternate La/Ba occupation within the planes. No magnetic moment is developed when the two Ba atoms are located on top of each other, i.e., along $\hat{z}$. This last result might seem surprising, since a finite magnetic moment is present next to a single Ba atom in the two other cases.

Therefore, it seems that inhomogeneous formation of doped holes in the vicinity of the impurity and the clustering of impurity atoms within the same plane are important ingredients for the formation of magnetic moments on Cu atoms and apical O sites. This conclusion is corroborated by the fact that no magnetism is found when the virtual crystal approximation (VCA) is applied for $x = 1$. The missing charge on Ba sites relative to La sites is only partly taken from the Cu band, so E_F does not quite reach the high DOS region; thus, the system is below the Stoner limit for ferromagnetism. Eventually, when the Ba concentration becomes larger ($x \geq 1.5$), ferromagnetism appears in VCA calculations. Random oxygen vacancies, described by coherent potential approximation (CPA) calculations, will increase the DOS at E_F [25] and might help Stoner magnetism.

TABLE I. The calculated magnetic moments (μ_B per cell) for $La_2Ba_2Cu_2O_8$ for the 3 configurations of Ba positions. The occupations of Ba/La are denoted as "pl-1" for plane 1, "col-2" for the second column, etc.

pl-1, col-1	pl-2, col-1	pl-1, col-2	pl-2, col-2	m
Ba	Ba	La	La	0.00
Ba	La	La	Ba	0.09
Ba	La	Ba	La	0.20

Next, by using larger supercell calculations with Ba/La substitutions, we try to answer the question of whether local spontaneous magnetization is possible for hole doping corresponding to the most "overdoped" (actually meaning low doping for supercell calculations) high-T_c materials and thus whether FM can be responsible for the disappearance of superconductivity. For the large supercells with 16 f.u. (112-site cells), we present results for configurations with 4, 10, and 16 Ba sites distributed randomly or with a tendency of clustering on the 32 available La sites. We focus on the *clustered* configurations since they show enhanced spontaneous magnetization. The calculations with 4 Ba sites correspond to the interesting doping concentration $x = 0.25$.

We first consider the paramagnetic state for 4 and 10 clustered Ba atoms, where the DOS are calculated within a larger mesh of 125 k points. While the main DOS features with *random* distribution of Ba sites are close to a rigid band picture given by our VCA calculations and by the CPA results for $x = 0.14$ [25] and for $x = 0.30$ [26], the DOS for clustered configurations can be different. The results for the clustered cases are compared in Fig. 1 together with the DOS for the pristine phase La_2CuO_4

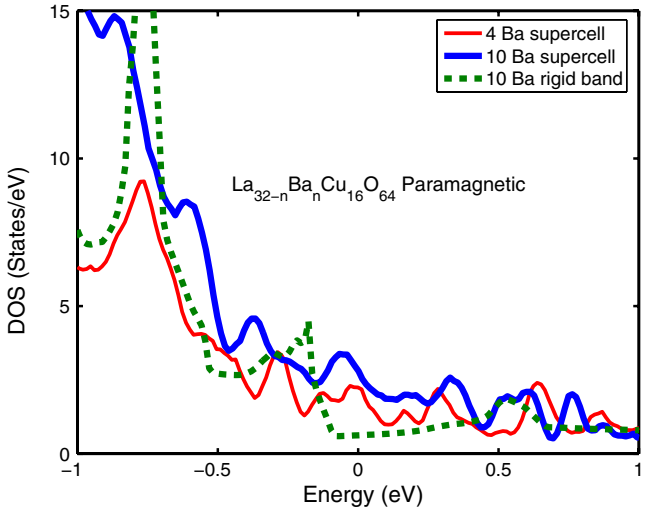

FIG. 1 (color online). Total paramagnetic DOS for the $La_{28}Ba_4Cu_{16}O_{64}$ and the $La_{22}Ba_{10}Cu_{16}O_{64}$ clusters compared to a rigid band model for La_2CuO_4, in which E_F is shifted to correspond to $x = 0.62$.

with a rigid band shift of E_F. As shown in Fig. 1, even a low concentration of Ba atoms is sufficient to induce band broadening and shifts of the DOS peaks towards E_F, whereas the rigid band model gives only a small DOS value at E_F. Broadening due to dilute substitution of La for Ba is not the whole story since the local DOS on individual Cu sites can also change dramatically during the self-consistent procedure of the spin-polarized calculations. Curiously, the spin-polarized calculations show that the largest local magnetic moments and their corresponding exchange splitting of the order of 1 mRy do not always occur on sites with large local paramagnetic DOS. Therefore, while the Stoner criterion seems to provide an overall indicator for possible magnetization, the paramagnetic DOS may be different from the actual shapes of majority and minority DOS in the FM phase. These strong nonlinear effects are also reflected by a slow convergence of the magnetic moment during the self-consistent procedure. Therefore, the results for the large supercell confirm that the charge transfer from the dopants to the CuO_6 octahedra adjacent to the Ba impurities and the resulting spontaneous magnetization cannot be modeled by using rigid band and Stoner schemes.

For the spin-polarized calculations, we also have studied the behavior of the magnetic moment as a function of the number of k points. The largest magnetic moments occur for simulations with only 4 k points. These calculations are analogous to models for FM nanodomains [7], where the pinning of E_F at DOS peaks is observed [27]. However, in order to simulate bulk properties, we have considered computations with 12, 27, and 125 k points. The total magnetic moments as a function of k points and different Ba configurations are displayed in Table II. The magnetic moments are localized on the Cu and apical O sites which are close to Ba sites, as in the case for the small cell. This can be seen in Figs. 2 and 3 of the supercell where the lengths of the arrows are proportional to the local magnetic moment on each site [28].

As shown in Fig. 2, both of the 16 Ba-site supercells, random and cluster, yield magnetic solutions. Therefore, a random distribution of Ba sites does not destroy magnetic solutions for very high Ba doping. Figure 2 confirms that the apical O sites close to Ba impurities have the highest magnetic moments.

Figure 3 illustrates the appearance of spontaneous magnetic moments for lower Ba concentrations. When decreasing Ba concentration to 10 clustered atoms, the apical O sites do not develop large magnetic moments as for the configurations with 16 Ba atoms. The effect of clustering is also seen in the case with four Ba atoms, i.e., for doping corresponding to the interesting range of doping for overdoped superconducting samples. With four clustered Ba atoms in the 112-site cell (3 next each other and the 4th one opposite in the next layer), it is possible to follow a contamination of the induced magnetic moment towards the Cu atoms in the second layer as shown in Fig. 3(b). About 60% of the total magnetic moment is on this Cu plane, which has fewer electrons than the first one. Interestingly, this self-consistent result has been obtained from a starting configuration where the magnetic moments were put near the Ba in the first layer of Cu. The magnetic moments on the O atoms (apical and planar) are generally very small at this low doping. This is in contrast to the result at larger doping, where apical sites could act as "links" between magnetic layers and thereby acquire magnetic moments. When the four Ba atoms are distributed randomly (i.e., not next to each other), the magnetic moment goes to zero (cf. Table II). This underlines the necessity for having a rather strong, local perturbation (a few Ba atoms within the same plane) in order to polarize neighboring Cu atoms.

Our results agree with the experimental findings that magnetization starts near $x = 0.22$ and corroborate the

TABLE II. The calculated magnetic moments (μ_B per cell) for $La_{(2-x)}Ba_xCu_2O_8$ as a function of k points for 5 configurations of Ba substitution with 16, 10, and 4 Ba on the 32 possible La positions. The averaged separation between energy levels is lower than the exchange splitting for the most dense k-point mesh, which indicates a sufficient k convergence.

x configuration	4 k	12 k	27 k	125 k
$x = 1.0$ cluster (16 Ba)	3.36	2.59	0.55	0.54
$x = 1.0$ random (16 Ba)	4.17	2.34	0.48	0.43
$x = 0.62$ cluster (10 Ba)	1.05	0.72	0.24	0.22
$x = 0.25$ cluster (4 Ba)	0.82	0.27	0.11	0.05
$x = 0.25$ random (4 Ba)	0.00	0.00	0.00	0.00

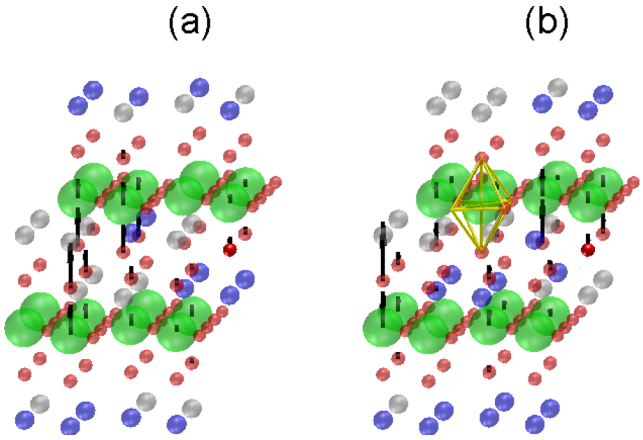

FIG. 2 (color online). Magnetic moments (arrows proportional to the size of the moments) on the atoms of the $La_{16}Ba_{16}Cu_{16}O_{64}$ (a) random and (b) cluster supercells (only nonequivalent atoms are shown). The (gray) small spheres are Ba atoms, the small (blue) spheres are La atoms, the large (green) spheres are Cu atoms, and the smallest (red) spheres are O atoms. The limits of an octahedron are outlined by yellow in (b). The calculations have been performed with 27 k points.

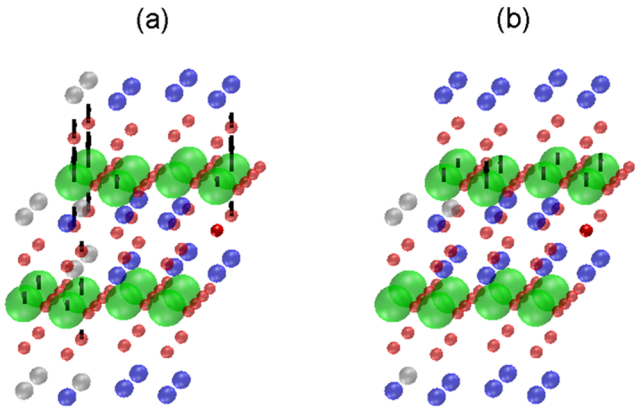

FIG. 3 (color online). Same as Fig. 2 for the (a) $La_{22}Ba_{10}Cu_{16}O_{64}$ and (b) $La_{28}Ba_4Cu_{16}O_{64}$ supercells. The arrows have been rescaled by a factor of 2 compared to Fig. 2 for clarity.

interpretation of neutron scattering data in terms of inhomogeneities such as Ba clusters and FM nanodomains [29]. The observed large increase of the magnetic moment with doping [29] may indicate a substantial clustering. In our calculations, the highest magnetic moment for alternate La/Ba layers at $x = 1$ (Table I) corresponds to $m = 1.6\mu_B$ per large cell instead of $m = 0.43\mu_B$ for the random configuration in Table II [30]. Furthermore, the case with $x = 0.25$ and 4 k points, which can simulate an isolated FM nanodomain as mentioned above, gives a magnetic moment of $m = 0.82\mu_B$, which is close to the experimental value $m = 0.5\mu_B$ given by Wakimoto *et al.* [29] for Sr doping that exceeds $x = 0.22$.

In conclusion, we have shown that the commonly used rigid band approximation is not appropriate for studies of doping in La_2CuO_4, at least not for delicate magnetic properties. Our calculations with different Ba compositions in small and large supercells show clearly different FM solutions as a function of the distribution of Ba atoms. Thus, not only the amount of doping (Ba concentration) but also the ordering of the Ba atoms is important. In particular, we have shown that ferromagnetism can be induced when the doping is high, and even at $x = 0.25$ if there is some clustering of the Ba atoms. In the latter case, only some regions near the Ba clusters are weakly polarized. The mechanism of ferromagnetism from Ba (or Sr) clusters could be responsible for the suppression of superconductivity in overdoped cuprates as suggested by Kopp, Ghosal, and Chakravarty [7].

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