Oxygen Stripes in $La_{0.5}Ca_{0.5}MnO_3$ from *Ab Initio* Calculations

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We investigate the electronic, magnetic, and orbital properties of $La_{0.5}Ca_{0.5}MnO_3$ perovskite by means of an *ab initio* electronic structure calculation within the Hartree-Fock approximation. Using the experimental crystal structure reported by Radaelli *et al.* [Phys. Rev. B **55**, 3015 (1997)], we find a charge-ordering stripelike ground state. The periodicity of the stripes, and the insulating magnetic structure, consisting of antiferromagneticaly coupled zigzag chains, are in agreement with neutron x-ray and electron diffraction experiments. However, the detailed structure is more complex than that envisaged by simple models of charge and orbital order on Mn d levels alone, and is better described as a charge-density wave of oxygen holes, coupled to the Mn spin/orbital order.

Understanding the physics displayed by manganite oxide compounds $R_{1-x}D_xMnO_3$ (R = rare-earth atom, D = divalent substituent) has stimulated much experimental and theoretical work [1]. Changing the composition x, they show a variety of phenomena, such as ferromagnetic (FM), antiferromagnetic (AFM), charge and orbital ordering (CO and OO) revealing that charge, spin and and lattice degrees of freedom are closely interrelated.

In the present Letter, we concentrate on the half-doped case of $La_{1-x}Ca_xMnO_3$ that has been extensively studied [2–6]. For $x = 0$, $LaMnO_3$, there is a collective Jahn-Teller (JT) distortion of the structure that gives rise to a splitting of the e_g levels. As a consequence of that, the structure is orthorhombic, the Mn e_g levels are singly occupied and all Mn ions are Mn^{3+}. For the other extreme doping ($x = 1$), $CaMnO_3$ is pseudocubic as the e_g levels are empty and Mn^{4+} does not couple to the lattice distortion. In $LaMnO_3$, the splitting of the e_g orbitals favors the cooperative JT distortions and the appearance of OO. This fact allowed Goodenough [7] and Kugel and Khomskii [8] to explain the magnetic structure of this compound. Their explanation assumed unpolarized O^{2-} ions and was based on the idea that magnetic ordering is dictated by the orientation of the orbitals involved.

The regime of intermediate doping is complex, magnetically and structurally, but even at the level of the *local* electronic structure there are several experiments that present contradictory results. Some of them claim a mixed valence picture of Mn^{3+} and Mn^{4+} while others found features that do not reconcile with this image. For example, by doing oxygen K edge electron-energy-loss spectra, it was concluded that carriers in $La_{1-x}Sr_xMnO_3$ ($0 \leq x \leq 0.7$) have a significant oxygen-p hole character [9]. Some x-ray absorption studies at the Mn K edge in Ca-doped $LaMnO_3$ revealed a picture that does not match with a mixture of Mn^{3+} and Mn^{4+} for intermediate dopings [10]. On the contrary, Tyson *et al.* [11] performed a Mn K_β x-ray emission experiment in the same com-

pound and found that their data was compatible with a Mn^{3+}/Mn^{4+} mixing for intermediate compositions. Similar contradictions have been found using neutron diffraction [12], photoemission and x-ray spectroscopy techniques [13]. These contradictory features motivate the need for a clarifying picture regarding the valence state of the Mn ions in manganite systems. One of the goals of the present Letter is to provide an *ab initio* quantum mechanical calculation to investigate the local electronic structure of the compound in order to establish the nature of the charge carriers.

In this Letter we report the theoretical finding of oxygen stripes in $La_{0.5}Ca_{0.5}MnO_3$ by means of an *ab initio* spin-unrestricted Hartree-Fock (HF) [14] study [15]. Our results were obtained by means of the code CRYSTAL98 [16] that uses a few localized basis functions per atom to solve self-consistently the HF equations. In the present Letter, the basis set for the different atoms are those optimized for previous calculations [17,18] and the crystal structure is taken from the experimental work reported by Radaelli *et al.* [3]. So, the present study takes into account the actual JT distortions and the size of the atoms involved. It is expected that the periodic HF approximation will correctly describe the physics involved in this system as it has been successful in describing other magnetic insulators as well as strongly correlated materials [14].

The crystal structure for $La_{0.5}Ca_{0.5}MnO_3$ can be indexed in space group $P2_1/m$ [3] with three inequivalent Mn atoms per unit cell. Two Mn ions are associated with JT distorted MnO_6 octahedra (that we will label as d1 and d2). Although in a similar environment of local O distortions, these two sites are not identical. The third Mn belongs to an almost undistorted octahedra. The cell of the crystal structure has one axis (b) longer than the other two ones (a, c). We will call *basal planes* the Mn-O planes perpendicular to the b axis. The magnetic ordering for this compound was coined CE-type [19]. It consists of FM zigzag chains that are coupled AFM (see Fig. 1).
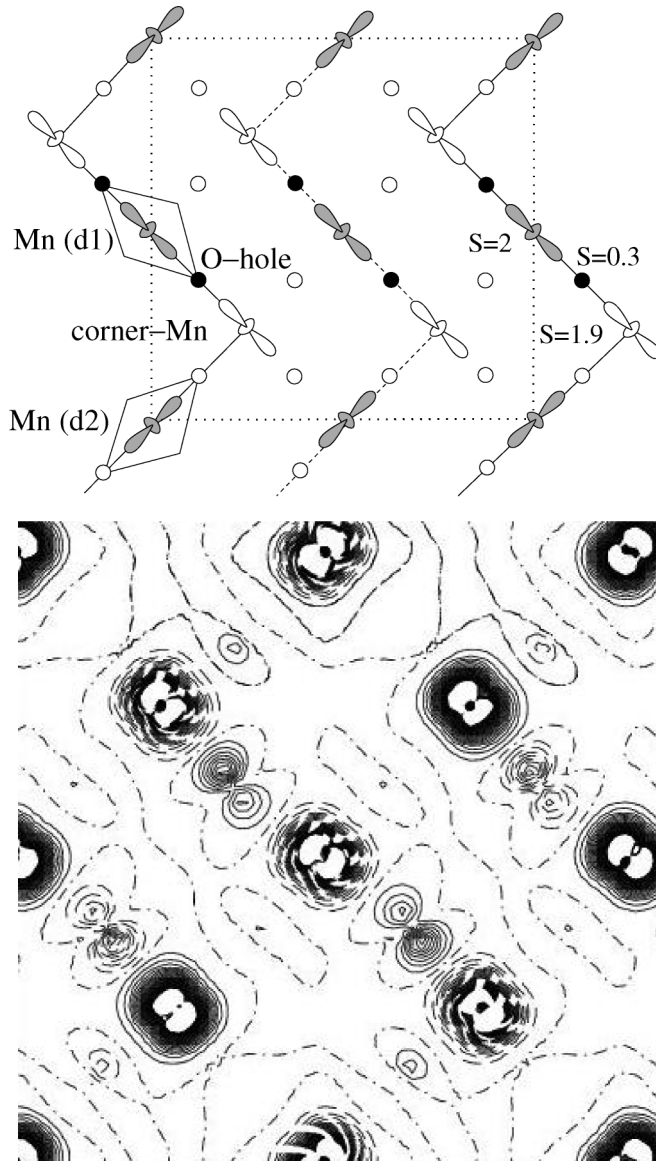
FIG. 1. Top panel: Sketch of the orbital ordering obtained from *ab initio* HF calculations. Mn(d1)/Mn(d2) are the Mn in the distorted octahedra d1/d2. The "corner-Mn" is shown. Shading indicates the spin polarization value (see Table I). Small circles represent the oxygens (black ones have spin-polarized holes). Solid and dashed zigzag lines indicate oppositely spin-polarized Mn species. The dotted line shows the unit cell used in all the calculations throughout this work. Bottom panel: Spin-density map of a basal plane (corresponding to the unit cell in the sketch). Continuous, dashed and dot-dashed isodensity curves correspond to positive, negative, and zero values, respectively. The CE-type magnetic ordering and the spin-polarized oxygen holes are clearly seen. Adjacent basal planes are AFM coupled and display stacking with identical Mn charge-orbital ordering.

As it was previously reported [17,20] for $LaMnO_3$ and $CaMnO_3$ within the HF approximation, Mulliken population analysis (MPA) gives charges for Mn and O ions that deviate substantially from the formal valence picture.

In these works, MPA results for $LaMnO_3$ give $Mn^{+2.2}$ and $O^{-1.7}$ to be compared with the formal values Mn^{+3} and O^{-2} whereas in $CaMnO_3$, $Mn^{+2.2}$ and $O^{-1.3}$ should be contrasted with Mn^{+4} and O^{-2}. However, the MPA for the spin values do not show such deviation. In $LaMnO_3$, the Mn spin was 1.98 [20] and in $CaMnO_3$, $\frac{3.2}{2}$ [17]; that is, very close to the formal valence spin values of 2 and $\frac{3}{2}$, respectively. In both cases, the spin for the O atoms was also close to the formal picture being mainly spin unpolarized. The origin of the difference between charge and spin values is the strong hybridization between Mn and O bands with the subsequent screening of Mn charge by electrons in the surrounding O atoms. In the half-doped case, we find that MPA also shows deviations from the formal valence picture with all Mn having about the same charge. For the oxygens, almost all of them have a formal charge close to $O^{-1.6}$, but there are some holes leading to $O^{-1.2}$, as we will detail further on.

Regarding the magnetic properties of this system, we found that the ground state is correctly predicted to have the CE-type ordering in agreement with neutron experiments [3,19]. The FM state and the *A*-type AFM state both have energies that are above the CE-type state by at least 1.1 and 0.9 eV per unit cell, respectively [21]. Presumably, the FM and *A*-type states have similar energies because the coupling between basal planes is weak.

We found that the ground state for the half-doped case is almost doubly degenerate. One of the solutions is visualized in the spin-density map depicted in Fig. 1, that clearly shows that the Mn ions display OO. As an aid to understanding the map, we draw in the same figure, a sketch of the corresponding orbital and crystal structure with shading showing the value of the spin polarization (S). Some oxygens have spin-polarized holes (see Table I). For the solution shown, holes are located on O atoms forming the long bonds of one of the distorted octahedra d1. The other (nearly degenerate) solution has oxygen holes instead along the long bonds of octahedra d2, with the corner-Mn orbital always in the direction of the O hole [22]. So, within the HF approximation, not just the Mn ions but also the oxygens play an important role. Indeed, as seen in Table I, charge modulation occurs principally on the oxygens rather than on Mn atoms.

TABLE I. Mulliken population values for the different atoms. The spin values for the Mn *d* orbitals are $t_{2g} = 1.4$, $d_{x^2-y^2} = 0.1$, $d_{3z^2-r^2} = 0.5$ for all of them.[a]

	Mn(d1)	Mn(d2)	Corner-Mn	O hole[b]	La	Ca
Charge	+2.1	+2.2	+2.1	−1.2	+2.9	+1.9
Spin	2.0	2.0	1.9	−0.3	0.0	0.0

[a]Local system of reference on each Mn, with *z* axis along the direction of the zigzag.
[b]The remaining oxygens have charge −1.6 and are weakly polarized.

The origin of the spin-polarized O holes can be understood in terms of the OO. For the analysis, we will consider only the atoms within a zigzag chain because the oxygens between chains are unpolarized (which is consistent with the AFM coupling between adjacent Mn). As can be seen in Fig. 1, the OO around Mn(d2) resembles LaMnO$_3$. Along the long bond of d2, we found no spin-polarized O holes which is consistent with Goodenough's ideas. However, around Mn(d1) the OO is different. In the long bond of d1, both Mn and O orbitals lie along the same line allowing for a transfer of charge from the O to the Mn, and rendering the O with a hole [23]. Because of exchange, this O hole has opposite spin to its two adjacent Mn ions.

As the spin-polarized oxygens are always AFM aligned with the neighboring Mn spin, the Mn-O complex forms a state analogous to the Zhang-Rice singlet in the cuprates [24]: the corner-Mn with the O hole forms a low spin state that gives a total $S \approx \frac{3}{2}$ (see Fig. 2). This connects to the usual models of d-orbital occupancy alone, where a hybrid Mn-O state stands in place of a Mn^{4+} ion. Since we find $S = 2$ for the remaining Mn atoms, they match the conventional picture of Mn^{3+} ions. So, although the chemistry is quite complex involving holes on some oxygens, due to the strong hybridization they are not independent degrees of freedom and the system should be viewed in terms of hybridized bands, possibly supporting the use of simplified single-band models.

The breaking of symmetry due to the localization of holes on oxygens in only one of the distorted octahedra appears to highlight the very small symmetry breaking in
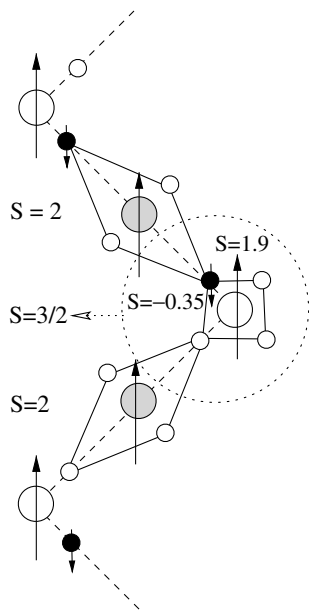

FIG. 2. Detail of a zigzag chain showing the low-spin state in manganites that is analogous to the Zhang-Rice singlet in cuprates.

the experimental crystal structure, where slightly different octahedra d1 and d2 have been reported [3]. Namely, in the a-c plane, the octahedra have long Mn-O distances of 2.07 and 2.06 Å and short Mn-O distances of 1.93 and 1.92 Å, respectively. However, we performed a relaxation by increasing the distance between the corner-Mn and O hole by 4% and the energy went down by 0.5 eV per unit cell, suggesting that a full relaxation is needed. It is worth asking if a further refinement can be performed taking into account the features suggested by our results. In fact, a recent refinement for the structure of Pr$_{0.6}$Ca$_{0.4}$MnO$_3$ [12] produces local ordering not dissimilar to the results of our model.

We now compare our results with electron-microscopy experiments (EM). As can be seen in Fig. 1, the CO and OO doubles the pseudocubic unit cell in one direction (vertical in Fig. 1) as reported in EM [4]. Note that the unit cell is further doubled in the horizontal direction due to the magnetic ordering although this cannot be explicitly seen in EM. It is important to note that either of the doubly degenerate solutions (either holes on d1 or holes on d2) produce identical periodicity for the diffraction pattern. In a real sample, there will always be some perturbation to stabilize one of the solutions.

In experiments, although La and Ca are on average randomly distributed, little is known about local arrangement within a range of a unit cell. We investigated this issue by checking the influence of different distributions for La and Ca within the planes just above and below the basal ones. We found that if the concentration of Ca is higher in the region above a particular octahedron (thus enhancing the symmetry breaking between d1 and d2), then holes locate in that octahedron and the energy is lowered by 3.8 eV per unit cell. This result suggest that the local environment is important and should be taking into account in future refinements.

Our picture is supported by an analysis of the density of states (DOS) (Fig. 3). In the valence band, the oxygens on d1 show a net down polarization (yet the other oxygens are almost unpolarized) and the spin-polarized contribution of each type of Mn is essentially up. The top of the valence band is mainly populated by oxygen bands showing the charge-transfer insulator character of this system. The spin-polarized holes just at the bottom of the conduction band indicate that the origin of the gap is probably the localization of the charge produced by the oxygen-stripes that develop in the system, as a charge-density wave (CDW).

In conclusion, we performed an *ab initio* study for the half-doped case of La$_{1-x}$Ca$_x$MnO$_3$ considering the experimental structure [3,19] and working within the HF approximation. In contrast to the conventional model of CO that produces insulating behavior by the alternation of Mn^{3+} and Mn^{4+}, our model yields an insulator because of ordering of O holes. Nevertheless, the spin character is exactly as predicted by the conventional models, because
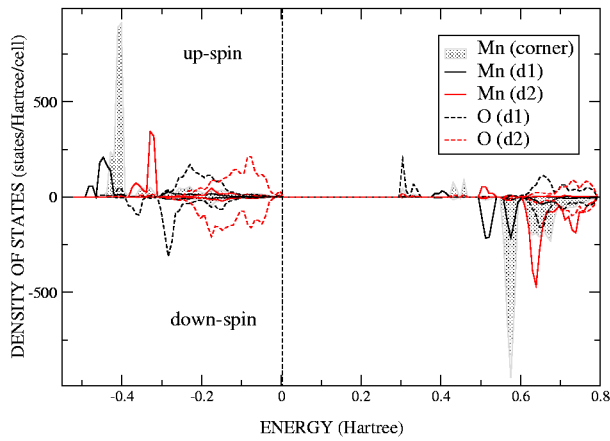
FIG. 3 (color online). DOS projected onto the atoms of a zigzag chain. The dotted line marks the Fermi energy. Indicated between parentheses is the octahedron to which each atom belongs.

each O hole is bound into a local low-spin state with the neighboring corner-Mn ion. The essential physics might be described with an effective Hamiltonian involving only Mn bands, but this issue requires further investigation [25]. Interestingly, we find that this hybridized low-spin state further orders in a broken-symmetry CDW with AFM order. The unit cell and the periodicity of the oxygen stripes are in agreement with neutron diffraction experiments. However, the O-hole density is substantial and not obviously compatible with the very small difference between d1 and d2 octahedra reported in Ref. [3]. Since the (La,Ca) disorder will favor locally broken-symmetry states, it is likely that these short scale fluctuations will restore the average symmetry of d1 and d2. Future work should allow the structure to relax within a theoretical calculation or to get a further refinement of the experimental crystal structure for $La_{0.5}Ca_{0.5}MnO_3$.

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