Oxygen-stripes in La$_{0.5}$Ca$_{0.5}$MnO$_3$ from ab initio calculations

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(October 28, 2018)

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 stripe-like ground state. The periodicity of the stripes, and the insulating CE-type magnetic structure 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.

PACS numbers: 75.47.Lx, 75.10.-b, 71.27.+a, 71.45.Lr

Understanding the physics displayed by manganite oxide compounds R$_{1-x}$D$_x$MnO$_3$ (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), anti-ferromagnetic (AF), charge and orbital ordering (CO and OO) revealing that charge, spin and and lattice degrees of freedom are closely interrelated.

In the present work, we concentrate on the half-doped case of La$_{1-x}$Ca$_x$MnO$_3$ 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 pseudo-cubic 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$_x$MnO$_3$ (0≤$x$≤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 $K\beta$ x-ray emission experiment in the same compound 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], photo-emission 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 work 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 work, 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 3 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)
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]. Due to exchange, this O-hole has opposite spin to its two adjacent Mn ions.

As the spin-polarized oxygens are always AF 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.

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

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 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 0.5eV 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 pseudo-cubic 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 can not 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 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$_3$.

The authors are indebted to Iberio de P. R. Moreira for helpful assistance with the CRYSTAL code and fruitful discussions. We are grateful for valuable suggestions from M. Calderón, N. Mathur, D. Khomskii, V. Heine, and especially L. Colombi Ciacchi. V. F. acknowledges support from the National Research Council of Argentina (CONICET) and Fundación Antorchas (Argentina). M. D. T. thanks Royal Society for support. P.B.L. acknowledges support from EPSRC.

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