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ScienceDirect
Journal of Magnetism and Magnetic Materials 316 (2007) e734–e737
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

First principle calculations of charge ordering in manganites

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Abstract

Electronic structure calculations were performed on the compound $La_{0.5}Ca_{0.5}MnO_3$ to study the relationship between the magnetic ordering, the charge ordering and the geometry of the compound. Charge ordering is intimately related to the magnetic ordering. An antiferromagnetic ordering induces charge disproportionation via a Jahn–Teller distortion. A full disproportionation in Mn^{3+}/Mn^{4+} occurs for the experimental geometry and allows to predict the experimentally found antiferromagnetic insulating state.
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PACS: 75.30.Mb; 75.50.Pp; 71.20.−b

Keywords: Manganites; Charge ordering; Ab initio calculations

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1. Introduction

Transition metal oxides, and manganites in particular, have received considerable attention in the last few years. The phenomena of colossal magnetoresistance [1], together with other interesting magnetic and electronic structure properties has produced an ever increasing knowledge in the field since the pioneering studies of the fifties. In particular, the series $La_{1-x}Ca_xMnO_3$ is one of the most thoroughly studied. It presents colossal magnetoresistance at $x = 0.33$ and different magnetic phase transitions with doping. It is specially interesting at half-doping because of the formation of the CE-type [2] (ferromagnetic zigzag chains coupled antiferromagnetically) magnetic phase with possible appearance of charge and orbital ordering. The origin of this behavior will be analyzed by means of ab initio calculations in this paper.

It is still a matter of debate whether charge ordering occurs with a full disproportionation between Mn^{3+} and Mn^{4+} ions or a so-called Zener polaron state takes place with all the Mn ions in an $Mn^{3.5+}$ state [3,4]. Also, the driving forces for any of these behaviors is under dispute and the relative importance of a Jahn–Teller distortion and the strong correlations by an on-site Coulomb repulsion between the d electrons of the cations is still uncertain.

2. Computational details

We have performed electronic structure calculations with the WIEN2k software [5] that uses a full-potential, all-electron method based on the density functional theory utilizing the augmented plane wave plus local orbitals (APW + lo) method [6]. We have introduced the effects due to the strong correlations by means of the LDA + U method [7] in the so-called "fully-localized limit" [8]. All the results presented are consistent for a wide range of U values, between 3 and 8 eV. For all the calculations presented, we converged our results with respect to the number of k-points in the irreducible wedge of the Brillouin zone and also with respect to $R_{mt}K_{max}$. The structure optimizations were carried out utilizing the generalized gradient approximation (GGA) [9].

3. Results

Due to the difficulties of studying the experimentally found CE-type magnetic structure, we have considered the C-, E- and A-type antiferromagnetic (AF) configurations. Both C- and E-type give equivalent results: same total

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0304-8853/$ - see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.jmmm.2007.03.215

energies, magnetic moments and optimized geometries. We also studied a ferromagnetic (FM) phase. For both the AF and FM cases, we optimized the geometry minimizing the forces in the structure and also the total energy. Both C- and E-type give equivalent results, same total energies, magnetic moments and optimized geometries. The obtained environments for the different Mn ions in the structure are summarized in Table 1. We can observe that very different environments for the inequivalent Mn ions in the structure are obtained depending on the magnetic ordering imposed. In the case of C- and E-type AF ordering, two structurally inequivalent Mn positions appear, an undistorted octahedron and an octahedron shortened along one axis. These different geometries imply different valence states of the Mn cations. However, for the A-type AF and FM cases, both positions are structurally equivalent. This is obtained without including strong correlation effects by the LDA + U method, there is a charge disproportionation produced by the Jahn–Teller distortion associated to a certain magnetic ordering. The magnetic moment is different for each environment, corresponding to different valence states of the Mn cation. In the FM case, both magnetic moments are the same, consistent with a Zener polaron picture of $Mn^{3.5+}$ ions coupled FM. The last column in Table 1 is the structure obtained by neutron diffraction by Radaelli et al. [10]. This gives for Mn2 an octahedral environment elongated along one axis.

We performed total energy calculations within GGA in the optimized geometries, being the A-type configuration the most stable one. With the structure by Radaelli et al., we performed also LDA + U calculations showing that the A-type configuration is also the most stable one (as we mentioned above, we did not study the ground state CE-type configuration). However, the A-type configuration obtained by a GGA minimization of the structure leads to a metallic state, even within the LDA + U approach, that is inconsistent with experiment. This is due to having FM planes where double exchange between $Mn^{3.5+}$ ions leads to a metallic behavior. This structure produces basically the same environment for the two Mn ions, formally in an $Mn^{3.5+}$ state. According to our calculations, the material is an insulator when it is in a charge disproportionated state (as in the structure by Radaelli et al.) but not if one only assumes an AF ordering but no charge disproportionation (as in the structure optimized considering an A-type AF ordering). The additional ingredient of an Mn^{3+}/Mn^{4+} charge disproportionation is required to open a gap around the Fermi level. From our calculations, we can observe that a certain degree of charge disproportionation is obtained only by a Jahn–Teller distortion produced by a certain AF ordering, but the introduction of the on-site Coulomb interaction leads to a different structure, elongated octahedron for the Mn^{3+} site (instead of shortened that comes out from GGA) and an almost full disproportionation into Mn^{3+} and Mn^{4+}. From these observations, we conclude that the structure by Radaelli et al. describes better the system than those obtained by a GGA-based structural minimization.

These findings agree with the observations by de Graaf et al. [11], they state that the driving force for charge disproportionation is the Jahn–Teller distortion. Popovic and Satpathy [12] also establish a similar picture to ours, they say that the most important term is due to the Jahn–Teller distortion but that some degree of disproportionation can be due to on-site Coulomb repulsions.

Table 1
Mn-O distance for the three different structures considered

Distances (Å)	C- and E-type AF	A-type AF	FM	Radaelli
Mn1–O	1.92 × 4	1.93 × 2	1.92 × 2	1.91 × 6
	1.93 × 2	1.96 × 4	1.95 × 4	
Mn2–O	1.91 × 2	1.91 × 2	1.92 × 2	1.92 × 4
	2.00 × 4	1.96 × 4	1.95 × 4	2.05 × 2

The geometries optimized considering an FM, different AF orderings and the structure obtained by Radaelli et al. [10]. Each distance is given with its multiplicity.

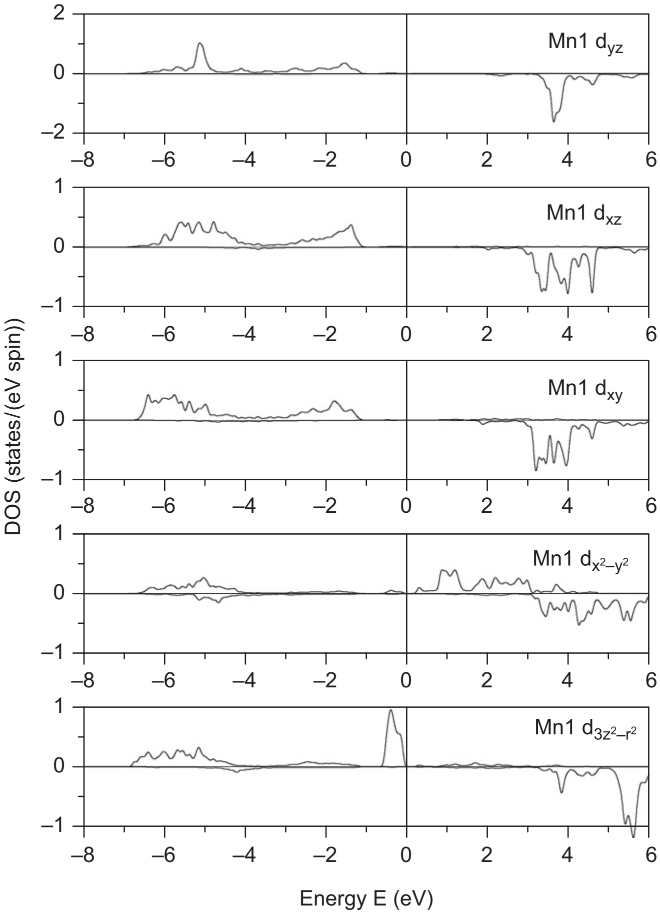

Fig. 1. Spin-up and spin-down partial density of states of the d levels of the Mn^{3+} ion in an AF phase using the structure by Radaelli et al.

However, other authors like van den Brink et al. [13] state that the driving force for charge ordering are the on-site Coulomb interactions. Our calculations show the importance of these for getting the correct distortions of the octahedra surrounding the cations, but some degree of disproportionation can be obtained without introducing these interactions. Also, this charge disproportionated state is not inherent to the CE-phase since we obtain it without introducing such a phase in the calculations but it is somehow related to it because an A-type configuration, without including strong correlation effects, leads to a non-disproportionated state.

This full disproportionation can be analyzed better with the aid of the density of states (DOS) plots shown in Figs. 1 and 2. These show the partial DOS for the d-levels of the so-called Mn1 (Mn^{3+}) and Mn2 (Mn^{4+}). The levels are oriented such that the z-axis goes along the elongated axis of the octahedron for the case of Mn^{3+} and along the crystallographic c-axis for the Mn^{4+} ion. The results shown were obtained in an A-type AF ordering with the structure by Radaelli et al., that includes two inequivalent atoms of each kind in the unit cell, that are coupled AF.

Figs. 1 and 2 show the material in an AF charge disproportionated state is an insulator. It can be observed that the degree of disproportionation is almost total. For the Mn^{3+} (Fig. 1), the $d_{x^2-y^2}$ orbital is unoccupied. Some small occupancy of the e_g levels is due to the hybridizations with surrounding oxygens. For the Mn^{4+} case (Fig. 2), two holes in the spin-up channel can be observed: one in the $d_{3z^2-r^2}$ level and another one in the $d_{x^2-y^2}$ orbital, i.e., the e_g levels are fully unoccupied, as expected for a d^3 configuration in an almost undistorted octahedron.

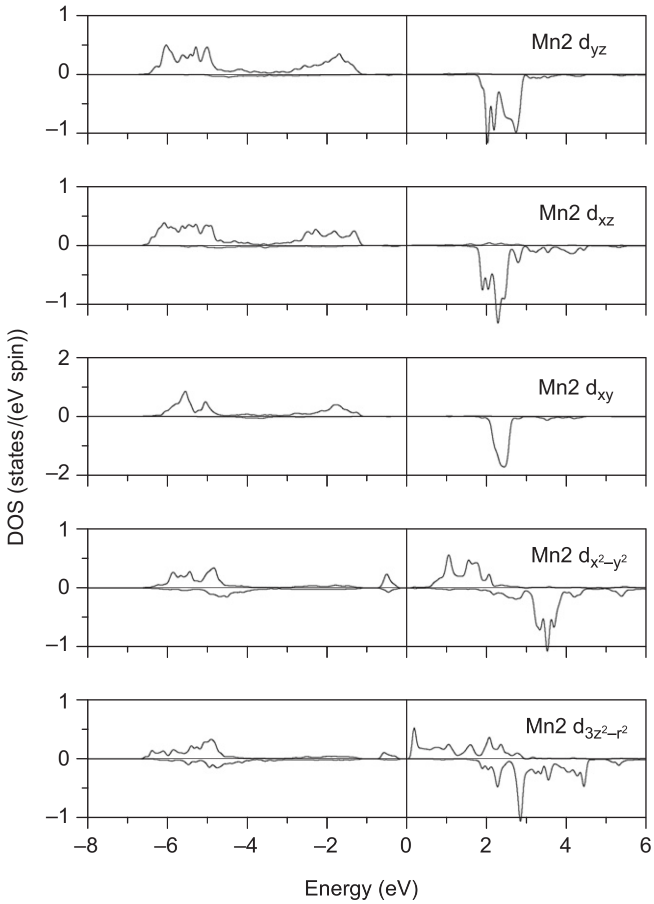

Fig. 2. Spin-up and spin-down partial density of states of the d levels of the Mn^{4+} ion in an AF phase using the structure by Radaelli et al.

We observe the effects due to charge disproportionation in the DOS of the Mn ions, and also in the values of the magnetic moments of these cations, in contrast to other studies [14] that associate the charge disproportionation to the oxygen cloud.

4. Conclusions

We have presented in this paper some electronic structure calculations of the geometrical implications of charge ordering in $La_{0.5}Ca_{0.5}MnO_3$. The main driving force for charge ordering is a Jahn–Teller distortion produced by the onset of an AF magnetic coupling. For the case of an FM phase, no charge disproportionation is expected and a wide e_g band crosses the Fermi level leading to a metallic state based on a double exchange process between $Mn^{3.5+}$ atoms. The on-site Coulomb repulsion is the additional ingredient that leads to a full disproportionation between Mn^{3+} and Mn^{4+} ions in the AF phase, that yields the correct insulating state. This is the structure found experimentally by Radaelli et al., that is more stable than the charge ordered state we could obtain without including strong correlation effects by a structural optimization within GGA.

The authors wish to thank F. Rivadulla for fruitful discussions, the CESGA (Centro de Supercomputación de Galicia) for the computing facilities and also the Xunta de Galicia, University of Santiago de Compostela and the Ministry of Science and Education of Spain for the financial support through Grant and project no. MAT2004-05130, respectively.

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