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## A hybrid-exchange density functional study of Ca-doped $\text{LaMnO}_3$

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In this work, hybrid-exchange density functional theory calculations are carried out to determine the effects of A-site doping on the electronic and magnetic properties of the manganite series  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ . This study focuses on the nature of the ground state for an ordered Ca distribution. We show that the hybrid exchange functional, B3LYP, provides an accurate and consistent description of the electronic structure for  $\text{LaMnO}_3$  and  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ . The magnetic ground states for the compositions studied are predicted correctly and comparisons have been made to available experimental data. This provides a basis for a first principles description of the magnetocaloric effect in  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ . © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4794877>]

### I. INTRODUCTION

Manganites with a general formula  $\text{R}_{(1-x)}\text{A}_x\text{MnO}_3$  (R being rare earth and A earth alkaline elements) are perovskites, which display a range of interesting phenomena, such as high-temperature superconductivity,<sup>1,2</sup> colossal magnetoresistance (CMR),<sup>3-5</sup> and the magnetocaloric effect (MCE).<sup>6-8</sup> A fundamental feature of manganites is the strong interplay between the spin, charge, orbital, and lattice degrees of freedom. This leads to a complex phase diagram, consisting of a rich variety of crystallographic, magnetic, and electronic phases.<sup>9-11</sup> These phases are dependent on the doping concentration  $x$  and variables, such as temperature, pressure, and electric/magnetic fields. As a consequence of the effects of strong electron correlation, a microscopic understanding of the physics underlying the properties of manganites has not yet been achieved.

The  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  series undergoes a phase transition from a low temperature ferromagnetic metallic (FM-M) to a high-temperature paramagnetic insulating (PM-I) phase for  $0.2 < x < 0.5$ .<sup>12</sup> The nature of the low-temperature FM-M phase in these compounds was discussed by Zener,<sup>13,14</sup> who proposed that this behaviour is driven by the double-exchange (DE) mechanism. Zener's DE model involves spin coupling between  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  next-nearest-neighbor ions with the conduction electrons mediating the interaction. For this series of manganites, the majority of quantum mechanical simulations has been performed on the parent compound,  $\text{LaMnO}_3$  (see Ref. 15 and references therein for a systematic review), and  $x = 0.5$ .<sup>16-18</sup> On the other hand, very few first principle studies have been carried out to investigate the intermediate compositions. The  $x = 1/4$  and  $x = 1/3$  compositions have been studied within the conventional local spin density approach (LSDA), for a simplified cubic perovskite structure,<sup>19</sup> and the generalized gradient approximation (GGA) for the orthorhombic perovskite structure.<sup>20</sup> Other first principle

studies<sup>21</sup> (for the end members) have focused on the *ad hoc* local density approximation with Hubbard U (LDA+U) method to treat on-site Coulomb interactions in a mean-field approximation.

In this paper, we present a comparative theoretical investigation of the effects of A-site doping on the electronic and magnetic structure of the manganite compositions with  $x = 0$  and  $x = 0.25$ , using hybrid-exchange density functional theory (DFT) calculations. Electron exchange and correlation are approximated using the B3LYP hybrid-exchange functional, since it is well documented that it provides an accurate and consistent description of the electronic structure of localized and strongly correlated systems.<sup>22-32</sup>

### II. COMPUTATIONAL DETAILS

All DFT calculations have been performed using CRYSTAL09,<sup>33</sup> a code based on the expansion of the crystalline orbitals as a linear combination of a local basis set (BS) consisting of atom centred Gaussian orbitals. The Mn, O, and Ca atoms are described by a triple valence all-electron BS: an 86-411d(41) contraction (one s, four sp, and two d shells), an 8-411d(1) contraction (one s, three sp, and one d shells), and an 8-65111(21) contraction (one s, three sp, and two d shells), respectively; the most diffuse  $sp(d)$  exponents are  $\alpha^{\text{Mn}} = 0.4986(0.249)$ ,  $\alpha^{\text{O}} = 0.1843(0.6)$  and  $\alpha^{\text{Ca}} = 0.295(0.2891)\text{Bohr}^{-2}$ . The La basis set includes a pseudopotential to describe the core electrons, while the valence part consists of a 411p(411)d(311) contraction scheme (with three s, three p, and three d shells); the most diffuse exponent is  $\alpha^{\text{La}} = 0.15\text{Bohr}^{-2}$  for each s, p, and d.<sup>24</sup> The B3LYP hybrid-exchange functional has been used for all calculations, which consists of a 20% exact Fock exchange.

### III. RESULTS

The experimental lattice parameters of the most stable (crystallographic/magnetic) phases for  $\text{LaMnO}_3$  and  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  are given in Table I. These geometries

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TABLE I. Experimental lattice vectors for the orthorhombic parent and doped ( $x = 1/4$ ) compounds. The ground state magnetic structures are given in the second column.

Compound		a (Å)	b (Å)	c (Å)
LaMnO <sub>3</sub>	AFM (A)	5.730	7.672	5.536
La <sub>0.75</sub> Ca <sub>0.25</sub> MnO <sub>3</sub>	FM	5.470	7.734	5.489

have been determined from neutron powder diffraction measurements.<sup>34,35</sup> The corresponding *Pnma* orthorhombic crystallographic cells are shown in Figure 1, where **b** is the longest vector. Mn ions are sixfold coordinated with O ions, which form an octahedral cage around the Mn, shown in Figure 1(a). The substitutionally disordered structure of La<sub>0.75</sub>Ca<sub>0.25</sub>MnO<sub>3</sub> has been approximated by an ordered Ca distribution, where a La atom has been replaced by a Ca atom in the unit cell of LaMnO<sub>3</sub>. The ionic radius mismatch between La and Ca leads to a contraction in **a** and **c** of 4.54% and 0.85%, respectively, while an expansion of 0.81% occurs in the **b** lattice vector.

The magnetic phases for LaMnO<sub>3</sub> and La<sub>0.75</sub>Ca<sub>0.25</sub>MnO<sub>3</sub> with corresponding spin density maps are shown in Figures 1(c) and 1(d). LaMnO<sub>3</sub> has an A-type ordering of the spins, which consists of ferromagnetic MnO<sub>2</sub> planes coupled antiferromagnetically along the **b** axis. This implies that both ferromagnetic and antiferromagnetic interactions exist between the Mn spins, mediated by O. Coherent orbital ordering occurs due to a cooperative Jahn-Teller (JT) distortion. The calculated energy difference between the AFM A-type and FM configurations for LaMnO<sub>3</sub> is 35.3 meV and the magnetic moment for the FM phase is 4.00  $\mu_B$ , per formula unit (FU). In the case of La<sub>0.75</sub>Ca<sub>0.25</sub>MnO<sub>3</sub>, the unit cell of the parent

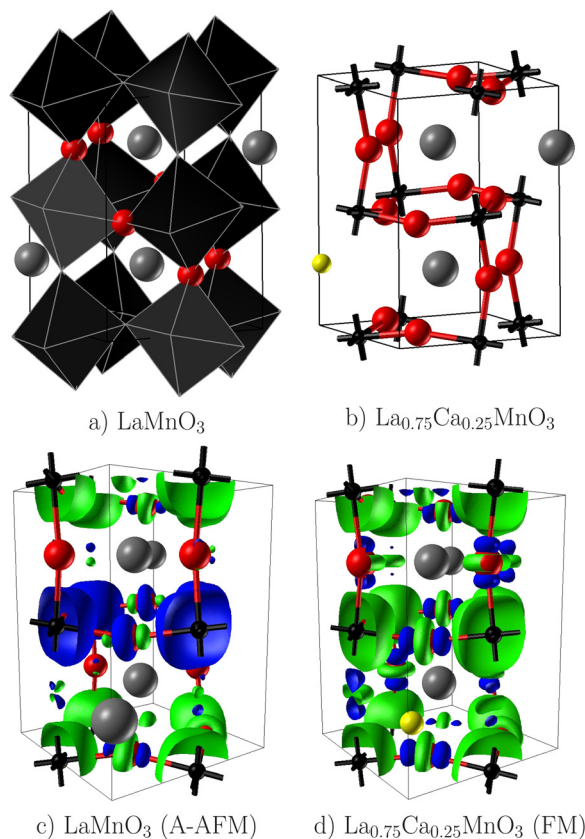


FIG. 1. Crystallographic cells at the geometries indicated in Table I are shown in (a) and (b). Large (grey), medium (red) and small (black) spheres correspond to the La, O and Mn atoms, respectively, in (a); the additional atom (yellow) in (b) and (d) is the Ca atom. Isovalue surfaces of the calculated spin density are shown in (c) and (d). The spin isosurface values are as follows: Green is 0.005 (spin up) and blue is  $-0.005$  (spin down), in units of  $|e|/\text{Bohr}^3$ .

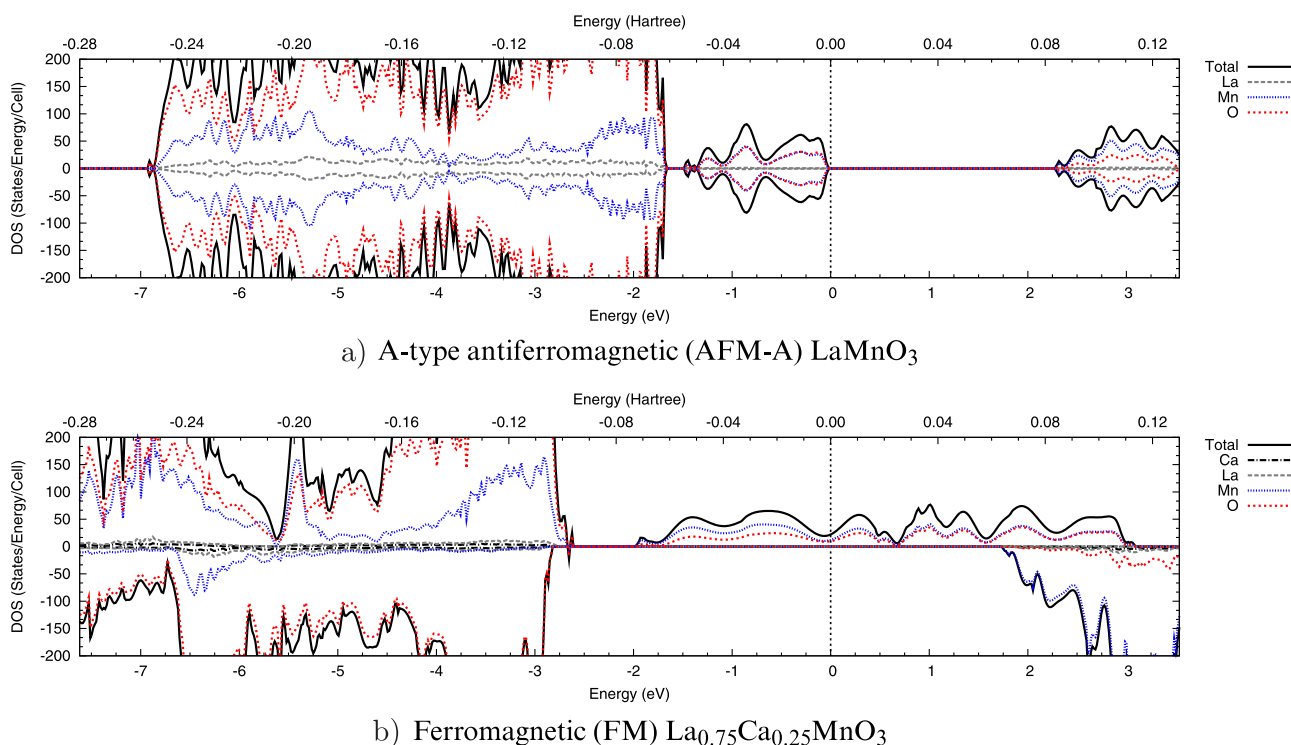


FIG. 2. Total density of states with projections on the Ca, La, Mn, and O atoms; the Fermi level is at 0 eV.



compound is doped with a hole when a La atom is replaced by a Ca atom. In Figures 1(c) and 1(d), it can be seen that the magnetic coupling switches from antiferromagnetic to ferromagnetic. The energy difference between the FM and AFM A-type configurations for this composition is 105.6 meV/FU and the magnetic moment for the FM phase is  $3.75 \mu_B/\text{FU}$ .

In order to analyse further the effects of Ca doping on the electronic properties, the total and projected electronic density of states (DOS) are shown for  $\text{LaMnO}_3$  and  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  in Figure 2.  $\text{LaMnO}_3$ , the parent compound, is an insulator with an indirect band gap of 2.3 eV as shown in Figure 2(a). This is comparable with the reported value of 1.7 eV (Refs. 36 and 37) from photoemission and x-ray-absorption (XAS) studies of  $\text{LaMnO}_3$ . The JT distorted Mn ions have a formal 3+ valence state and a  $3d^4$  configuration in the ionic model: Three electrons fill the  $t_{2g}$  orbitals that lie low in energy and one electron occupies an  $e_g$  orbital, which is higher in energy.  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  is completely spin polarized at the Fermi level. This is in agreement with the half-metallicity reported experimentally from scanning tunnelling spectroscopy measurements.<sup>38</sup> The band gap in the minority spin states is 4.57 eV. The lower valence band DOS is mainly attributed to the O 2p and Mn 3d bands, which overlap for both compositions. This is also true for  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$  at the Fermi energy in the majority spin states and therefore the bonding is not purely ionic.

#### IV. CONCLUSIONS

We have performed hybrid-exchange DFT calculations for  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  at  $x=0$  (in the A-type AFM configuration) and  $x=0.25$  (in the FM configuration), in the orthorhombic (*Pnma*) structures. Isovalue surfaces of the calculated spin density show that Ca leads to a switching of the sign of the exchange interaction. In addition, the electronic density of states shows that the Ca induces a delocalization of the majority spin  $e_g$  states leading to half metallicity, from an insulating phase in  $\text{LaMnO}_3$ . The present study demonstrates the reliability of the description of the hybrid B3LYP functional for strongly correlated systems, such as manganites. This work represents a good starting point for further much more computationally demanding investigations, aimed at determining the effect of a disordered Ca distribution on the structural, magnetic, and electronic properties of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ .

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