

# Ab initio investigation of the magnetic states of $\text{Ca}_2\text{MnO}_4$ and $\text{Ca}_2\text{MnO}_{3.5}$

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## Abstract

An analysis of the electronic and magnetic properties of  $\text{Ca}_2\text{MnO}_4$  and  $\text{Ca}_2\text{MnO}_{3.5}$  is carried out within local spin density functional theory using the augmented spherical wave method. From energy differences between the hypothetical magnetic configurations both systems are found to be insulating antiferromagnets in the ground state with a  $\sim 1$  eV gap. However we identify an intermediate half metallic ferromagnetic state with the Hund's rule expected moments for  $\text{Mn}^{\text{IV}}$  ( $3 \mu_B$ ) and  $\text{Mn}^{\text{III}}$  ( $4 \mu_B$ , high spin HS configuration), respectively. The latter result of moment magnitude finds support in recent experimental evidence of  $\text{Mn}^{\text{III}}$  bismuth oxide as a ferromagnet in its ground state. This is characterized by a small density of states (DOS) magnitude of itinerant states in spin ( $\uparrow$ ) channel pointing to a metallic-like behavior as it is experimentally evidenced. For both  $\text{Ca}_2\text{MnO}_4$  and  $\text{Ca}_2\text{MnO}_{3.5}$  the chemical bonding characteristics are resolved for the two spin channels. Relationship to colossal magnetoresistive compounds is proposed. © 2004 Elsevier B.V. All rights reserved.

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## 1. Introduction

For many years now a reliable account of the electronic and magnetic properties of a large majority of materials has been shown to be achievable within the density functional theory (DFT) [1,2] in its local spin density approximation (LSDA) for the effects of exchange and correlation [3–5]. The LSDA, built within the scheme of a homogeneous electron gas, accounts for exchange at a local level (contrary to Hartree–Fock approach, see exact exchange alternative scheme [6]) in an overall collective electron framework. Looking more particularly into transition metal oxide systems, a relevant question arises then as to whether an itinerant elec-

tron treatment is the right framework for the study of such highly correlated states as those of 3d electrons. As a matter of fact several drawbacks have been found while applying the LSDA to account for the insulating behavior of monoxides such as NiO [7] (although the metallization of insulating “FeO” induced by high pressure could be analyzed within the LSDA [8]). As an alternative, the “LDA +  $U$ ” correction to the correlation was proposed [9–11]. It introduces an electrostatic repulsion parameter ( $U$ ) which adds up to the LDA potential to account for the magnetic system within a localized picture (Hubbard type). This is particularly helpful for narrow bands whose electrons are strongly correlated such as in oxide insulators based on 3d elements. As a consequence there is a better account of the insulating properties with an opening of the gap at the top of the valence states which is otherwise

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underestimated (see Section 4.2.2 as well). LDA functional is nevertheless reliable when the material shows a metallic behavior as it will be shown here. In this context several manganese oxides with perovskite  $\text{AMnO}_3$  ( $A = \text{La, Ca, Sr}$ ) and pyrochlore  $\text{B}_2\text{Mn}_2\text{O}_7$  ( $B = \text{Sc, Y, Tl}$ ) derived structures have been investigated in recent years by us and others mainly for their giant magnetoresistive (GMR) properties [12–15] as well as for the coexistence of ferromagnetic and ferroelectric properties such as in  $\text{BiMnO}_3$  [16,17]. Further, recent studies were devoted to half-doped (equal amounts of divalent  $\text{Ca}^{2+}$  and trivalent  $\text{Ln}^{3+}$ ) manganese oxides which present simultaneous  $\text{Mn}^{\text{III}}$  and  $\text{Mn}^{\text{IV}}$  ions for Jahn–Teller and charge ordering characteristics [18,19].

Concerning  $\text{CaMnO}_3$ , precise determinations of energy differences between the experimental and hypothetical magnetic configurations concluded to the experimentally observed ground state of an antiferromagnetic (AF) insulator, albeit with a small gap [20]. Among the examined magnetic states, a half metal ferromagnetic (HMF) intermediate phase slightly above the (AF) ground state was evidenced. Such a behavior was experimentally observed from spin resolved photoelectron spectroscopy for  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  [21]. Interestingly a reduced manganese oxidation state:  $\text{Mn}^{\text{III}}$ , i.e. starting from  $\text{Mn}^{\text{IV}}$  can be induced through oxygen deficient compositions while keeping the divalent cationic sublattice. This is the case of  $\text{CaMnO}_{2.5}$  obtained from  $\text{CaMnO}_3$  [22]. The experimental data on the magnetic structure of  $\text{CaMnO}_{2.5}$  point to a high spin (HS) state of  $\text{Mn}^{\text{III}}$ . Our investigation within the LSDA concluded to the same magnetic state of manganese and to a half metallic ferromagnet ground state which is only at a slightly lower energy ( $\Delta E = 2.2 \times 10^{-3}$  eV per formula unit) than the AF state. This led us to suggest that both magnetic states are accessible within the magnetic phase diagram [23]. Similarly  $\text{Ca}_2\text{MnO}_{3.5}$  was obtained from  $\text{Ca}_2\text{MnO}_4$  [24], the first member of the Ruddlesden–Popper family of manganites  $(\text{Ln,AE})_{n+1}\text{Mn}_n\text{O}_{3n+1}$  ( $\text{Ln}$ : trivalent rare-earth,  $\text{AE}$ : divalent alkaline earth) [25] which has gained renewed interest in view of the outstanding properties of manganese oxides [26]. In this context the aim of this work is to present an original approach to the magnetic states and chemical bonding characteristics of  $\text{Ca}_2\text{MnO}_4$  and  $\text{Ca}_2\text{MnO}_{3.5}$  systems in the context of ab initio computations based on the local spin density functional. Complementary computations are provided here for the magnetic structure of recently evidenced ferromagnetic perovskite  $\text{BiMnO}_3$  [27,31].

## 2. Computational framework

Within the density functional theory in its local spin density implementation, we have used the all-electron augmented spherical wave (ASW) method [28,29] in a

scalar relativistic implementation [30].  $\text{Ca}(4s)$ ,  $\text{Mn}(4s, 3d)$  and  $\text{O}(2p)$  states were treated as band states, therefore being part of the set of trial wave functions used to perform the variational procedure. Energetically low lying  $\text{O}(2s)$  states were considered as core states. The only external inputs to the calculations are the crystal structure and parameters, as well as the atomic numbers dispatched into core and valence electrons. The calculations are hence fully ab initio and self-consistent. However the use by the ASW method of the atomic sphere approximation (ASA) introduces further approximations. Firstly the ASA assumes central potentials which lead to a spherical averaging of the electron density; this can be a severe approximation for systems which need full account of the potential in order to correctly account for their physical properties. Further the ASA assumes overlapping spheres whose volume equals the volume of the unit cell. This approximation is unproblematic for closely packed structures like metals and intermetallics but for a loosely packed structure such as that of the several classes of oxide systems (perovskite-type,  $\text{K}_2\text{NiF}_4$ -type,  $\text{GdFeO}_3$ -type ...), empty spheres (ES) need to be introduced to represent the interstitial space and to avoid an otherwise too large overlap between the actual atomic spheres. ES are “pseudo atoms” with zero atomic number. They receive charges from the neighboring atomic species and allow for possible covalency effects within the lattice. ES were introduced within the structural setups of the oxide systems under study here. The Brillouin zone integration was done using an increasing number of  $k$  points within the irreducible wedges of the respective crystal structure (cf. Table 1) to ensure convergence of the results with respect to the  $k$ -space grid. A sufficiently large number of  $k$  points was used to ensure for convergence for variational energy and charge, i.e. until  $\Delta E \sim 10^{-8}$  Ryd. and  $\Delta Q \sim 10^{-8}$  electron in the iterative process. This is compulsory if sufficiently accurate values of the magnetic moments and of the total energies are to be compared, especially when differences are to be analyzed.

### 2.1. Description of the chemical bonding

The results obtained from the DFT are relevant as to quantities regarding the magnitudes of the magnetic moments, the nature and energy position of the states with respect to the Fermi level. However one needs a more elaborate of information about the nature of the interaction between atomic constituents as well as the respective quantum states involved. Such information can be provided in the framework of the overlap population (OP) which involves the overlap matrix leading to the so-called crystal orbital overlap population (COOP) [32] or alternatively introducing the Hamiltonian based population COHP (crystal orbital Hamiltonian population) [33]. Both approaches provide a qualitative description

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