

Ab initio electronic structure and magnetism in Sr_2XMoO_6 (X = Fe or Co) double perovskite systems: a GGA and GGA+*U* comparative study

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2006 J. Phys.: Condens. Matter 18 11291

(<http://iopscience.iop.org/0953-8984/18/49/020>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 14:52

Please note that [terms and conditions apply](#).

***Ab initio* electronic structure and magnetism in Sr₂XMoO₆ (X = Fe or Co) double perovskite systems: a GGA and GGA + *U* comparative study**

Daniel Stoeffler¹ and Corina Etz²

Institut de Physique et de Chimie des Matériaux de Strasbourg (UMR 7504 CNRS),
23 rue du Loess, BP 43, F-67034 Strasbourg Cedex 2, France

E-mail: Daniel.Stoeffler@ipcms.u-strasbg.fr and cae@cms.tuwien.ac.at

Received 30 August 2006, in final form 18 October 2006

Published 22 November 2006

Online at stacks.iop.org/JPhysCM/18/11291

Abstract

Using the full potential linearized augmented plane wave *ab initio* method, we investigate bulk magnetic properties of Sr₂XMoO₆ (X = Fe, Co) double perovskites by comparing the results obtained with the generalized gradient approximation (GGA) and GGA + *U* methods in order to discuss their magnetic configuration in relation with the experiments. We show that both methods lead to significantly different results and that a good agreement with experimental results—antiferromagnetic insulator for X = Co—can be obtained only when the GGA + *U* method is used. For X = Fe, we exhibit the role played by oxygen vacancies in the stabilization of a negative magnetic moment on the Fe antisite with preserved half-metallicity. We show that such a negative moment can be obtained only when an oxygen vacancy occurs in the direct neighbourhood of the Fe antisite with the GGA + *U* method.

1. Introduction

The potential use of magnetic oxide as electrode in spintronic devices has stimulated theoretical investigations, in terms of magnetic ordering and spin dependent band structure, aiming to predict their capability to spin polarize a current [1, 2]. Sr₂FeMoO₆ (SFMO) double perovskite (DP) is a candidate for such materials due to (i) its half-metallic (HM) property (it act as an insulator for one spin channel and as a metal for the other one) and (ii) its ferromagnetic ordering up to 415 K. However, the preparation of these oxides being hard to achieve without structural and chemical imperfections, the expected properties have not yet been clearly exhibited.

¹ Author to whom any correspondence should be addressed.

² Present address: Center for Computational Materials Science (CMS), Gumpendorferstraße 1A, A-1060 Vienna, Austria.

Recently, theoretical studies [3–5] have investigated the role played by antisites (ASs) using two extreme approaches: the double exchange model (DEM) and density functional theory (DFT) band structure calculations based on local density or generalized gradient (GGA) approximations. To summarize, they gave contradictory results: following DEM (respectively DFT), the magnetic moment carried by an Fe AS should be opposite to (aligned with) the ones carried by regular Fe sites, preserving (destroying) the HM feature. Consequently, the DEM won experimentalists' favour by explaining the lower than expected saturation magnetization in terms of a small number of Fe ASs ($10 \mu_B$ being lost per Fe AS) while preserving the 100% spin polarization capability. In this paper, we simulate the occurrence of ASs, O vacancies (O^*) and of (AS, O^*) pairs and show that taking electronic correlation into account in the DFT within the GGA + U approach changes significantly the results of the DFT calculations for SFMO and shows a nice agreement with experiment for Sr_2CoMoO_6 (SCMO).

2. Methodology

We have calculated self-consistently the band structure for the considered DP systems in the full potential augmented plane wave formalism (FLAPW) in the FLEUR implementation³ and taking core, semi-core and valence states into account. Because the generalized gradient approximation (GGA) usually reinforces the HM character (for example see [7] and the SFMO section of this paper) and gives more accurate structural properties than the usual local density approximation, we use directly the GGA without and with the Hubbard contribution (GGA + U). In agreement with the literature on the GGA + U method [6], we use $U_{Fe} = 4$ eV, $U_{Co} = 5$ eV and $J_{Fe} = J_{Co} = 0.89$ eV. Moreover, because the relative stability of magnetic configurations in SCMO will depend on very small energy differences (as we will discuss later), we have varied the U_{Co} (3, 4 and 5 eV) and J_{Co} (0.78, 0.89 and 1.00 eV) parameters without having noticed a significant alteration of the main conclusions and without change of the most stable magnetic solution [8].

All calculations are carried out for a set of increasing \mathbf{k} points until no variation into the main results is reached. More precisely, for the cases without O vacancies we used up to 84 or 75 special k -points in the irreducible wedge of the Brillouin zone, and for the case with O vacancies we used up to 48 special k -points during the self-consistent calculations. An energy convergence of 10^{-5} Hartree is reached and, for successive sets of \mathbf{k} points with increasing numbers, the variation of the total energy was smaller than 2×10^{-4} Hartree. Finally, the densities of states are determined using a few hundred \mathbf{k} points and are slightly smeared only outside bandgaps.

For the perfect SFMO case, we consider the experimental tetragonal cell within the $I4/mmm$ space group, with the lattice parameters $a = 5.58$ Å and $c = 7.90$ Å [9] containing two formula units (fu) (see table 1). For cases with imperfections, the same cell is used (the Fe AS is built by replacing one of the two Mo atoms by one Fe atom) with a lower symmetry space group when O^* are considered (one O atom along the z Fe–O–Mo link is removed). For the perfect SCMO case, the experimental cell with tilted octahedra along the z axis is used within the $I4/m$ space group with $a = 5.565$ Å and $c = 7.95$ Å [10] (see table 1). In the present work, only the a and c cell parameters are varied and, depending on the used symmetry, the internal positions of the atoms remain fixed and equal to the values given by table 1. Calculations of the structural parameters allowing a full relaxation of internal coordinates are under progress but are far from being achieved and will be published in a forthcoming paper. Preliminary results

³ FLEUR is an implementation of the full potential linearized augmented plane wave method freely available at <http://www.flapw.de> funded by the European Research Network Ψ_k and managed by Professor S Bluegel.

Table 1. Internal atomic position for all inequivalent sites for the two structures considered.

(<i>I4/mmm</i>)/(<i>I4/m</i>) (SFMO or SCMO)/(SCMO)	Site	<i>x</i>	<i>y</i>	<i>z</i>
Sr	4d	0/0	0.5/0.5	0.25/0.25
Fe or Co	2a	0/0	0/0	0/0
Mo	2b	0/0	0/0	0.5/0.5
O1	4e	0/0	0/0	0.2500/0.2589
O2	8h	0.2500/0.2895	0.2500/0.2296	0/0

for the perfect case show that the internal relaxation plays a limited role and does not affect the main conclusions of the present work, more significant modifications being expected for the imperfect cases.

3. SFMO

Previous works [11, 12] have shown the importance of the Hubbard contribution by combining electronic structure calculations and photoemission spectroscopy results. However, its role in the stability of ferrimagnetic (Fi) versus ferromagnetic (F) ordering around an Fe AS has not been considered up to now.

As a preliminary study, we have varied the *a* and *c* cell parameters for a set of (*a*, *c*) points on a grid within the *I4/mmm* symmetry in order to get the values of *a* and *c* minimizing the total energy by interpolating the calculated values. Surprisingly, the energy minimum is obtained for very similar (*a*, *c*) values for the GGA (*a* = 5.640 Å, *c* = 7.971 Å) and for the GGA + *U* (*a* = 5.646 Å, *c* = 7.977 Å) methods. Consequently, a fair approximation of the energy minimum is obtained for *a* = 5.65 Å and *c* = 7.98 Å, corresponding to an overestimation of 1.4% and 1.0% of the *a* and *c* parameters relative to the experimental values [9]. However, the local magnetic moments are slightly enhanced with the GGA + *U* method ($M_{\text{tot}} = 4 \mu_{\text{B}}/\text{fu}$ with $M_{\text{Fe}} = 3.99 \mu_{\text{B}}$ and $M_{\text{Mo}} = -0.41 \mu_{\text{B}}$) as compared to the GGA method ($M_{\text{tot}} = 4 \mu_{\text{B}}/\text{fu}$ with $M_{\text{Fe}} = 3.81 \mu_{\text{B}}$ and $M_{\text{Mo}} = -0.30 \mu_{\text{B}}$) as a consequence of the enhanced bandgap in the majority spin band. Note that, for these parameters, a local spin density approximation calculation gives a metallic behaviour with reduced magnetic moments ($M_{\text{tot}} = 3.92 \mu_{\text{B}}/\text{fu}$ with $M_{\text{Fe}} = 3.66 \mu_{\text{B}}$ and $M_{\text{Mo}} = -0.24 \mu_{\text{B}}$). Table 2 summarizes all these results.

From the point of view of the band structure, the main change when using the GGA + *U* method relative to GGA is a lowering (respectively an increase) of the energy of occupied (unoccupied) states, resulting in an enhancement of the main gap in the majority spin band from 0.6 to 1.7 eV (table 3). However, for both methods, the Fermi level lies approximately 0.5 eV (0.55 for GGA and 0.48 for GGA + *U*) below the bottom of the conduction band, in reasonable agreement with the measured half-gap of 0.7 eV [13]. This gap enhancement has a direct consequence on the predicted transport properties of epitaxial SFMO films deposited on SrTiO₃ (STO) [14]. Indeed, using GGA, a possible transition from metallic to half-metallic SFMO has been predicted when the cell is constrained by epitaxy on STO, SFMO being metallic for *c* smaller than 7.900 Å + 23.614 (*a* = 5.524 Å). This separation line crosses the experimental *c*(*a*) curve for *a* = 5.54 Å and *c* = 8.16 Å, corresponding approximately to a deposited SFMO thickness of 38 nm. In contrast, with GGA + *U*, SFMO remains HM in the range of *a* and *c* values explored. A spin resolved photoemission experiment as a function of the deposited SFMO thickness could consequently allow us to prove the reliability of the use of GGA + *U* for such kinds of materials.

Table 2. Structural, magnetic and electronic properties of the studied cases using LDA, GGA and GGA + U methods. The cell parameters a and c are given in Å and have been obtained (i) by total energy minimization (Min.) in a single cell (SC) of 10 atoms (basic fu) or in a double cell (DC) of 20 atoms (double fu) or (ii) experimentally (exp.). The magnetic configuration (F or AF) and the electronic character at E_F (half metal (HM), metal (M) or insulator (I)) are given. Finally, the total magnetic moment M_{tot} (in μ_B for the given formula) and the local magnetic moments (in μ_B) for Fe, Co and Mo are also given.

	Method	a, c (origin)	Magn., elec.	M_{tot}	$M_{\text{Fe,Co}}, M_{\text{Mo}}$
Sr ₂ FeMoO ₆ <i>I4/mmm</i>	LDA	5.64, 7.97 (GGA Min.)	F, M	3.92	3.66, -0.24
	GGA	5.64, 7.97 (Min.)	F, HM	4	3.81, -0.30
	GGA + U	5.65, 7.98 (Min.)	F, HM	4	3.99, -0.41
Sr ₂ CoMoO ₆ <i>I4/mmm</i>	GGA	5.61, 7.93 (Min. SC)	F, HM	3	2.69, -0.15
	GGA	5.61, 7.95 (Min. DC)	F, HM	3	2.69, -0.15
	GGA	5.61, 7.95 (Min. DC)	AF, M	0	±2.62, ±0.06
	GGA + U	5.61, 8.02 (Min. DC)	F, HM	3	2.67, 0.05
	GGA + U	5.61, 8.02 (Min. DC)	AF, I	0	±2.68, ±0.02
Sr ₂ CoMoO ₆ <i>I4/m</i>	GGA	5.565, 7.95 (exp.)	F, HM	3	2.64, -0.06
	GGA	5.565, 7.95 (exp.)	AF, M	0	±2.65, ±0.02
	GGA + U	5.565, 7.95 (exp.)	F, HM	3	2.69, 0.04
	GGA + U	5.565, 7.95 (exp.)	AF, I	0	±2.69, ±0.02

Table 3. Total magnetic moment M_{tot} in μ_B for the given formula, bandgap in eV and magnetic ordering for the most stable solution of all seven situations considered in this work using GGA/GGA + U methods. The uppercase arrow gives the spin direction of the band presenting the gap ($\uparrow\downarrow$ means that the same gap is obtained for both directions), F, AF and Fi corresponding respectively to ferro-, antiferro- and ferrimagnetic configurations.

	M_{tot} (μ_B)	Bandgap (eV)	$E_{\text{Fi}} - E_F$ (meV/cell)	Magn. order
Sr ₄ Fe ₂ Mo ₂ O ₁₂	8.0/8.0	0.59 [↑] /1.71 [↑]	—	F/F
Sr ₄ Fe ₂ Mo ₂ O ₁₁	6.0/6.0	0.16 [↑] /1.40 [↑]	—	F/F
Sr ₄ Fe ₃ MoO ₁₂	11.0/13.5	metallic/metallic	710/78	F/F
Sr ₄ Fe ₃ MoO ₁₁	10.7/4.0	metallic/0.31 [↑]	360/ - 222	F/Fi
Sr ₄ FeMo ₃ O ₁₂	4.81/4.79	metallic/metallic	—	F/F
	M_{tot} (μ_B)	Bandgap (eV)	$E_{\text{AF}} - E_F$ (meV/cell)	Magn. order
Sr ₄ Co ₂ Mo ₂ O ₁₂ (<i>I4/mmm</i>)	6.0/0.0	0.69 [↑] /0.23 ^{↑↓}	117/-18	F/AF
Sr ₄ Co ₂ Mo ₂ O ₁₂ (<i>I4/m</i>)	6.0/0.0	1.41 [↑] /1.04 ^{↑↓}	142/-7	F/AF
Sr ₄ Co ₂ Mo ₂ O ₁₁	4.0/4.0	0.37 [↑] /1.59 [↑]	95/76	F/F

According to the previous section, for all following calculations we use now the experimental lattice parameters $a = 5.58$ Å and $c = 7.90$ Å [9]. For this crystalline structure, when one O* is introduced, the gap remains but, due to the broadening of the unoccupied Mo t_{2g} states—resulting from the splitting of the peak into two peaks, it is reduced by 0.45 eV. As a consequence of the preserved HM property, the total magnetic moment in the cell is reduced by $2 \mu_B$ (from 8 to $6 \mu_B$) because five (respectively three) electrons are removed from the majority (minority) spin band. Nearly all eight electrons removed with the vacancy from the muffin tin sphere of the removed O atom and from the interstitial volume, which become highly polarized (-0.6 (GGA)/ -0.8 (GGA + U) μ_B /cell) as compared to perfect SFMO for which it is nearly unpolarized. This leads us to the conclusion that O* may have a strong impact on the magnetic couplings into the whole cell.

In the cell we consider here for simulating the Fe or Mo antisite, one of the three Fe or Mo atoms is on an AS which gives a high AS concentration comparable to the highest value experimentally explored [15]. In this experimental work, the Mo NMR spectra have been found to be not affected when the AS concentration is varied from 28 to 3%, leading to the conclusion that the transferred hyperfine field (HF) on Mo sites can be neglected and that the measured HF is given only by the local Mo magnetic moment. Band structure calculations allow us to determine explicitly these local magnetic moments for varying situations: for instance, for Sr₄FeMo₃O₁₂ (SFMO[Mo AS]), the three inequivalent Mo atoms carry a local moment of -0.18 , 0.04 and $0.26 \mu_B$, showing clearly that this local moment is highly affected by imperfections. Whatever the used method is, Sr₄FeMo₃O₁₂ (SFMO[Fe AS]) and SFMO[Mo AS] are found to be metallic (figure 2 and table 3) and, consequently, the solutions with all Fe moments aligned are always the most stable. For the particular case of SFMO[Fe AS], the energy difference between solutions with opposite local moments on the AS is found to be strongly reduced when using GGA + U ($\Delta E(\text{Fi} - \text{F}) = 78 \text{ meV/AS}$) as compared to GGA ($\Delta E(\text{Fi} - \text{F}) = 710 \text{ meV/AS}$). However, a total energy difference of 78 meV/AS remains a large value and we believe that relaxations would not change the sign of this difference. Consequently, even if we relax the atomic degrees of freedom, the F solution is expected to remain the most stable and the Fi one remains hard to stabilize. This result confirms that stable ferrimagnetic (Fi) solutions involving only AS can scarcely be obtained by band structure calculations.

As previously discussed, oxygen vacancies may affect the magnetic couplings between Fe atoms. By combining AS and O* imperfections, in a Sr₄Fe₃MoO₁₁ (SFMO[Fe AS, O*]) cell, we get a most stable Fi and HM solution with the GGA + U method ($\Delta E(\text{Fi} - \text{F}) = -222 \text{ meV/AS}$), whereas it remains F and metallic with the GGA ($\Delta E(\text{Fi} - \text{F}) = 360 \text{ meV/AS}$). Consequently, we conclude that the occurrence of an oxygen vacancy at the octahedra of an Fe AS is nearly the only way to get a stable negative moment on the Fe AS. Moreover, because the half-metallic property is preserved in such a solution, we also get an agreement between the DEM and the band structure calculations concerning the stabilization of a negative magnetic moment on the AS. Because the Fe AS without an oxygen vacancy as neighbour carries a positive moment, only the fraction of Fe AS forming a pair with an oxygen vacancy gives rise to a magnetization reduction: our works point out that the relevant parameter for studying the occurrence of the Fi solution is not the concentration c_{AS} of Fe AS but the concentration c_{AS,O^*} of Fe AS and O* forming a pair of neighbours. If the occurrence of Fe AS results from excess Fe atoms in excess, each single AS adds $1.5 \mu_B$ to the total magnetization, whereas each AS and O* pair removes $8 \mu_B$. If it results from exchange between Fe and Mo atoms, each single AS adds $1.15 \mu_B$ to the total magnetization whereas each AS and O* pair removes only $3.6 \mu_B$. Experimentally, a slope around $-8 \mu_B$ per AS is found, corresponding to excess Fe AS and O* pairs. However, this would mean that each Fe AS forms a pair with an oxygen vacancy. *A priori*, it seems difficult to have $c_{\text{AS}} = c_{\text{AS},\text{O}^*}$ and, experimentally, no appreciable deviations to the nominal oxygen content have been found [16]. But this becomes more reasonable if we consider that $c_{\text{AS}} = 25\%$ corresponds to an O* concentration of $c_{\text{AS}}/12 = 2\%$. Consequently, only a few per cent of oxygen vacancies are required and, considering that they enhance the atomic mobility of the Fe and Mo atoms, it is highly probable that they form pairs with most antisites.

4. SCMO

Recently, SCMO DP, the Co analogue of SFMO, has been synthesized using a ‘*chimie douce*’ method and has been characterized by neutron powder diffraction [10]. The stoichiometric

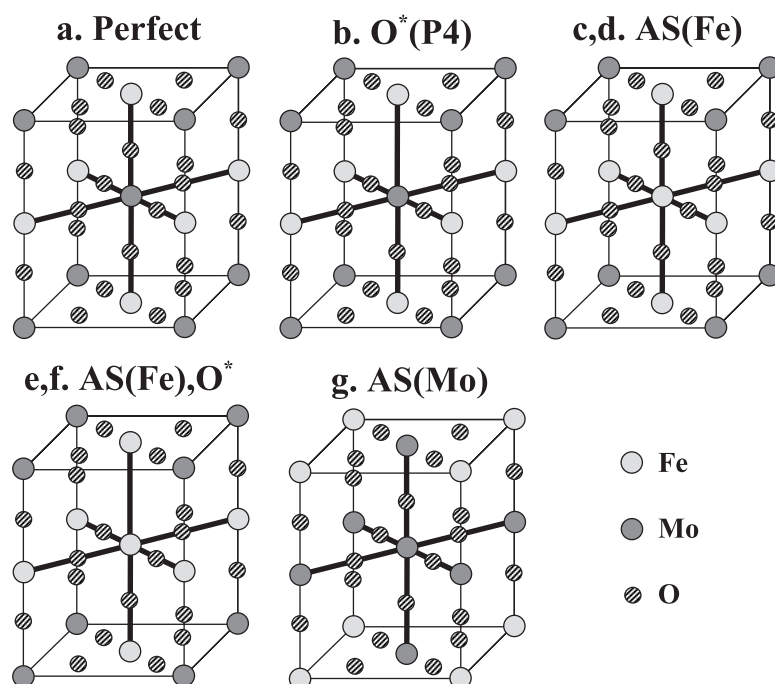


Figure 1. Schematic representation of the unit cells used in this work for SFMO: perfect case (a), with one oxygen vacancy (b), for an Fe antisite ((c), (d)), for an Fe antisite with one oxygen vacancy ((e), (f)) and for a Mo antisite (g). The Sr atoms are not shown and the antisite is at the centre of the cell.

samples are found to be antiferromagnetic (AF) with $T_N = 37$ K and insulating, whereas the reduction of these samples, leading to oxygen-deficient perovskites with the same crystal structure, gives rise to F domains with $T_C = 350\text{--}370$ K and a dramatic increase of the conductivity related to a large component of itinerancy for down-spin Mo t_{2g} electrons.

For the perfect SCMO case, we first consider the tetragonal cell within the $I4/mmm$ space group with the internal coordinates fixed at the values of table 1. With the GGA method, the total energy minimization into a single cell containing only one formula unit gives $a = 5.61$ Å and $c = 7.93$ Å. It is not surprising to find a slightly larger basal ab plane parameter than measured because the octahedra tilting affects more especially in plane Co–O–Mo bonds, leading to a reduction of the Co–Mo distance. For the investigation of the AF order, where two non-inequivalent Fe sites are required, we consider the tetragonal cell displayed by figure 1 contained 2 fu. With this cell, the energy minimum for the F and AF states is obtained for the same cell with $a = 5.61$ and $c = 7.95$ Å, in nice agreement with the result obtained in the single cell. We conclude that the error on the determination of the parameters with our approach is around 0.02 Å. With the GGA + U method, we obtain again the same cell for the minimal energy for both F and AF configurations with $a = 5.61$ Å and $c = 8.02$ Å. This shows that the c parameter is much more sensitive to the used method than the in plane a parameter. Table 2 summarizes again all these results. The total densities of states (TDOSs) for the F solution with the GGA are very similar to the one obtained for SFMO with a gap (ranging from -0.1 to 0.7 eV) around the Fermi level (E_F) in the up-spin DOS separating mainly Co occupied states from mainly Mo t_{2g} unoccupied States, whereas the down-spin DOS is metallic-like around E_F . As a consequence of this HM character, the total moment is equal

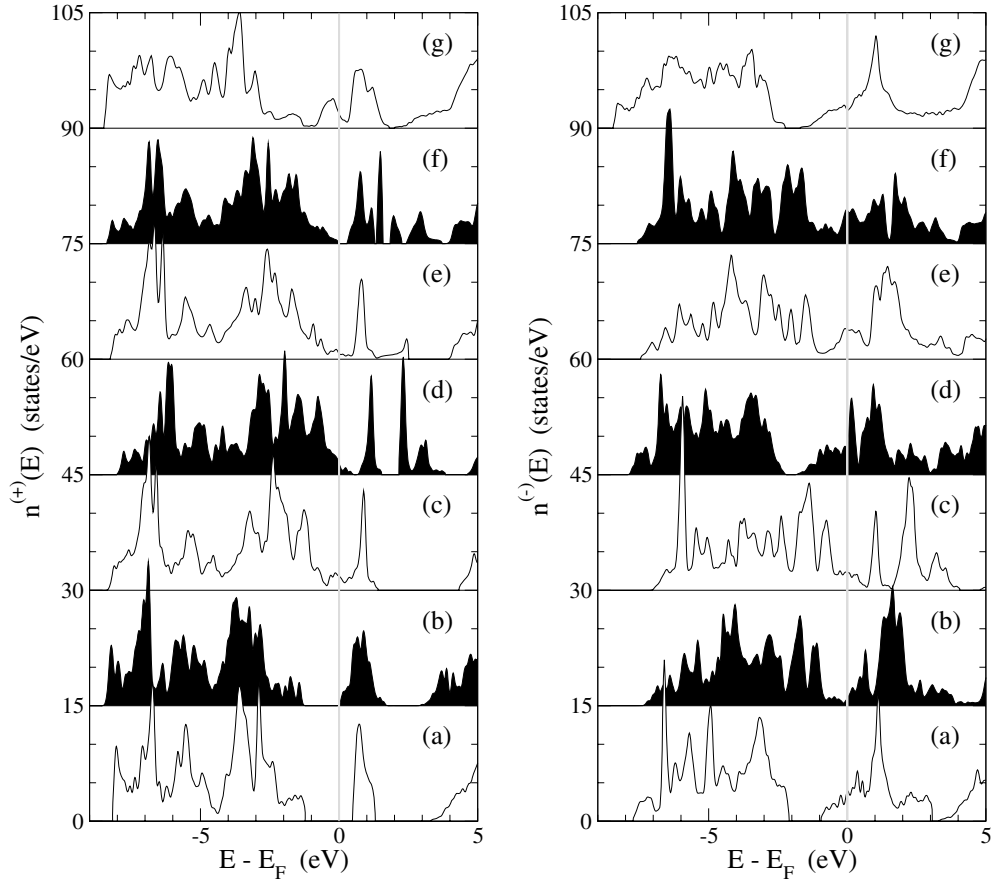


Figure 2. Total up (left) and down (right) spin densities of states for SFMO: perfect case (a), with one oxygen vacancy (b), for an Fe antisite having its local magnetic moment aligned (c) or opposite (d) to the regular sites, for an Fe antisite with one oxygen vacancy having its local magnetic moment aligned (e) or opposite (f) to the regular sites and for a Mo antisite (g). The densities have been offset by 15 states/eV and the vertical grey line corresponds to the Fermi level.

to $3 \mu_B/\text{fu}$. For the AF solution, built by considering a unit cell containing 2 fu with opposite magnetic moments on the two Co sites, we obtain a metallic behaviour around E_F . However, the F solution is found to be the most stable by 117 meV/2 fu cell. Consequently, the SCMO is found to be half-metallic and ferromagnetically ordered for the $I4/mmm$ structure with the GGA method. When the GGA + U method is used, we obtain significantly different results. Indeed, for the F solution, having also a total moment of $3 \mu_B/\text{fu}$, both spin TDOSs present a gap around E_F . A similar result is obtained for the AF solution, presenting a small gap (from -0.11 to 0.11 eV). However, the AF solution is found to be more stable by 18 meV than the F one. Consequently, the SCMO is found to be insulating and antiferromagnetically ordered for the $I4/mmm$ structure with the GGA + U method, this result being clearly more satisfactory when compared to the experiments.

For the experimental $I4/m$ crystal structure, we do not expect the main structures in the DOS to be affected but, because the four in plane ab Co–O–Mo bonds are no longer rectilinear, the interaction between Co and Mo states can be significantly changed, affecting directly the

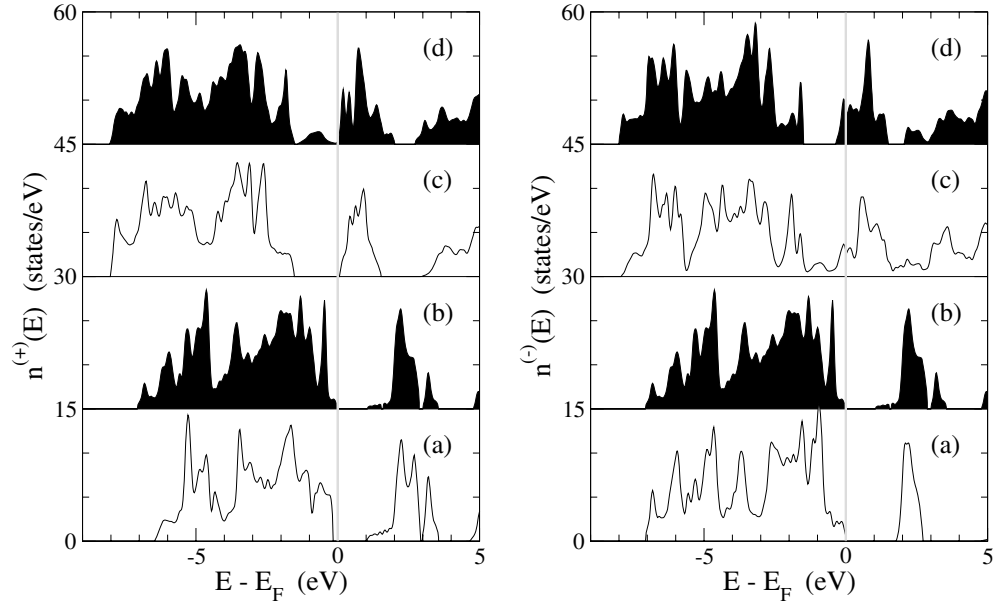


Figure 3. Total up (left) and down (right) spin densities of states for SCMO: perfect case ferromagnetically (a) and antiferromagnetically (b) ordered and with one oxygen vacancy ferromagnetically (c) and antiferromagnetically (d) ordered. The densities have been offset by 15 states/eV and the vertical grey line corresponds to the Fermi level.

gap between occupied Co and unoccupied Mo states. This is exactly what we obtain. With the GGA method, the TDOSs are very similar to the previous ones and present more narrow structures separated by larger gaps (for example, the gap around E_F in the spin-up TDOS for the F solution is nearly twice as large), indicating clearly more tight Co–O–Mo bonds. The AF solution is also found to be less stable than the F one by 142 meV. Surprisingly, this F solution is 457 meV less stable in the $I4/m$ crystal structure than the corresponding F solution in the $I4/mmm$ one. Consequently, the disagreement with the experimental results becomes more pronounced with the GGA method. Using the GGA + U method (figure 3), an insulating behaviour is obtained for both F and AF solutions with enlarged gaps as compared to the GGA, and the AF solution is also the most stable one by 7 meV. The major new result of this calculation is that the $I4/m$ crystal structure is 160 meV more stable than the $I4/mmm$ one.

Experimentally, for the oxygen-deficient samples, it has been shown that ferromagnetism is recovered and that the resistivity increases. Within the DEM, this can be understood by considering that the removal of O atoms adds two electrons to the delocalized charge per O^* and that a fraction of this additional electronic charge is gained by the Mo atoms in the vicinity of the vacancy. Consequently, 4d electrons become available on these Mo sites carrying a negative local magnetic moment and resulting in a double-exchange mechanism as in SFMO. We have done the calculation for $Sr_4Co_2Mo_2O_{11}$, corresponding to a much higher O^* concentration than the experimental one, starting from the experimental $I4/m$ cell and using a lower symmetry space group when removing one O atom of a Co–O–Mo link along the c direction. We get the F solution to be more stable than the AF one with both GGA ($\Delta E_{F-AF} = -95$ meV) and GGA + U ($\Delta E_{F-AF} = -76$ meV) methods. As expected, we recover clearly Mo states around the Fermi level and the magnetic moment on the Mo site having an O^* as neighbour is found to

be large ($-0.45 \mu_B$ for F and $-0.26 \mu_B$ for AF). Finally, the TDOS (figure 3) shows clearly that the stabilization of an F solution corresponds to a HM electronic structure, in perfect agreement with the observed increase of the conductivity for this situation.

Consequently, we found a complete agreement with experiments with the GGA + U method: the $I4/m$ crystal structure is the most stable, the perfect SCMO is an antiferromagnetic insulator and ferromagnetism is recovered for the oxygen-deficient structure. In the following, we consider only the results obtained with the GGA + U method for the discussion.

5. Discussion

For SFMO, in the DEM model, Fe³⁺ (3d⁵) ions carrying a $5 \mu_B$ magnetic moment are negatively coupled to Mo⁵⁺ (4d¹) ions carrying an $1 \mu_B$ magnetic moment via a super-exchange mechanism involving the O atom in between the Fe and Mo atoms. This explains well the F order obtained on the Fe sublattice by considering Fe–O–Mo–O–Fe chains where two successive Fe moments are negatively coupled to a common Mo moment. It also explains the HM property giving (i) a completely filled Fe 3d (t_{2g} and e_g) up-spin band split by super-exchange from the empty Mo 4d (t_{2g}) up-spin band by a gap and (ii) a partially filled Mo 4d (t_{2g}) down-spin band. Consequently, the single conduction electron in the down-spin 4d shell of Mo is at the origin of the HM and F states. Our explicit band structure calculations agree with the conclusions of the DEM (ferromagnetic half-metal with a total magnetic moment of $4 \mu_B/\text{fu}$) but not with the considered charge occupation. Indeed, by integrating the charge density in the muffin tin spheres, we get an occupation of 24.6 electrons for Fe carrying a moment of $4 \mu_B$ and an occupation of 38.7 electrons for Mo carrying a moment of $-0.4 \mu_B$, the configuration corresponding much more to Fe^{2.1+} (3d^{5.9}) and Mo^{3.5+} (4d^{2.5}) ions. Consequently, Fe–Mo hybridized states have to be considered: the gap in the up-spin DOS splits hybridized (mainly Fe(e_g)) fully occupied states from hybridized (mainly Mo(t_{2g})) unoccupied states and the partially occupied down-spin metallic band also consists of hybridized (Fe(t_{2g}) and Mo(t_{2g})) states. Considering SCMO, an insulating AF solution is found to be the most stable with our calculations. This agrees with the DEM only if we assume that we have Co²⁺ (3d⁷) ions carrying a $3 \mu_B$ magnetic moment and Mo⁶⁺ (4d⁰) ions carrying no magnetic moment. With such a configuration, no d electrons are available on the Mo site, giving the insulating behaviour, and no double exchange mechanism can take place for coupling the Co magnetic moments. Indeed, only a super-exchange mechanism can occur, involving two Co moments coupled through two directly linked O atoms of the octahedra surrounding the Mo atom situated at the corner of the Co–Mo–Co bond making a right angle. Instead of having the magnetic coupling dominated by Co–O–Mo–O–Co chains, like in SFMO, the coupling is dominated by Co–O–O–Co ones. Consequently, the two Co moments are negatively coupled, giving rise to an AF order. As for SFMO, this model does not agree with our explicit band structure calculations when considering charge occupations. We get an occupation of 25.8 electrons for Co carrying a moment of $2.7 \mu_B$ and an occupation of 38.9 electrons for Mo carrying a moment of $0.02 \mu_B$, the configuration corresponding much more to Co^{1.9+} (3d^{7.1}) and Mo^{3.6+} (4d^{2.4}) ions. However, a close look at the DOS shows that these occupied Mo states are very deep in energy (around -5 eV below the Fermi level) and there are effectively no Mo states available above -2 eV even if the configuration is not 4d⁰.

6. Conclusion

To summarize, we have shown that the use of the GGA + U method allows us to get a fair agreement between the calculated and observed magnetic and transport properties for SFMO

and SCMO, confirming that the present approach has the ability to describe accurately such kinds of systems. For SFMO, we have shown that Fe antisite and O vacancy pairs play an essential role for the occurrence of antialigned Fe magnetic moments while preserving the half metallic property. SCMO is an antiferromagnetic insulator for the most stable $I4/m$ crystal structure and it becomes half-metallic and ferromagnetic when oxygen vacancies are present. We have analysed our results using the double-exchange model and we have shown that both approaches lead to the same conclusions, but the DEM has to be used carefully and gives only trends.

Acknowledgments

The authors thank S Colis and A Dinia for stimulating discussions and the Centre d'Etudes du Calcul Parallèle et de la Visualisation (<http://www-cecpv.u-strasbg.fr>) of University Louis Pasteur for computing facilities. C Etz acknowledges the financial support from the ERASMUS program and the hospitality of the IPCMS.

References

- [1] Kobayashi K I, Kimura T, Sawada H, Terakura K and Tokura Y 1998 *Nature* **395** 677
- [2] Sarma D D 2000 *Phys. Rev. Lett.* **85** 2549
- [3] Saha-Dasgupta T and Sarma D D 2001 *Phys. Rev. B* **64** 064408
- [4] Solovyev I V 2002 *Phys. Rev. B* **65** 144446
- [5] Fang Z, Terakura K and Kanamori J 2001 *Phys. Rev. B* **63** 180407(R)
- [6] Solovyev I V and Dederichs P H 1994 *Phys. Rev. B* **50** 16861
- [7] Weht R and Pickett W E 1999 *Phys. Rev. B* **60** 13006
- [8] Etz C and Stoeffler D 2006 *Eur. Phys. J. B* submitted
- [9] Colis S, Stoeffler D, Mny C, Fix T, Leuvre C, Pourroy G, Dinia A and Panissod P 2005 *J. Appl. Phys.* **98** 033905
- [10] Viola M C *et al* 2002 *Chem. Mater.* **14** 812
- [11] Saitoh T *et al* 2002 *Phys. Rev. B* **66** 035112
- [12] Ray S *et al* 2003 *Phys. Rev. B* **67** 085109
- [13] Navarro J *et al* 2004 *Phys. Rev. B* **69** 115101
- [14] Fix T, Stoeffler D, Colis S, Ulhaq C, Versini G, Vola J P, Huber F and Dinia A 2005 *J. Appl. Phys.* **98** 023712
- [15] Wojcik M *et al* 2004 *Phys. Rev. B* **69** 100407(R)
- [16] Frontera C *et al* 2003 *Phys. Rev. B* **68** 012412