Interactions among magnetic moments in the double perovskites $Sr_2Fe_{1+x}Mo_{1-x}O_6$

J. Pilo [a], E. Carvajal [a,*], R. Oviedo-Roa [b], M. Cruz-Irisson [a], O. Navarro [c]

[a] Escuela Superior de Ingeniería Mecánica y Eléctrica-Culhuacán, Instituto Politécnico Nacional Av. Santa Ana 1000, México, D. F., C. P. 04430, México
[b] Programa de Investigación en Ingeniería Molecular, Instituto Mexicano del Petróleo Eje Central Lázaro Cárdenas Norte 152, México, D. F., C. P. 07730, México
[c] Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México A.P. 70-360, México, D. F., C. P. 04510, México

ABSTRACT

It is well known that every double perovskite shows a characteristic magnetic behavior, as a consequence of the interactions among the magnetic moments associated with the atoms in their cells; at the same time, the electric and magnetic properties of the bulk double perovskite Sr_2FeMoO_6 are well characterized. In this work we studied the iron rich compounds $Sr_2Fe_{1+x}Mo_{1-x}O_6$, using a supercell to model such concentrations that made Fe richer perovskites by $\pm 66.6\%$ and $\pm 200\%$. Starting from the stoichiometric double perovskite, and modifying the Fe/Mo ratio in the compound, the study of these materials were based on the calculation of the magnetic moment at each atom, as well as the partial density of states.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The radical changes suffered by many properties when materials are spatially confined could be the better support to the fact that research on materials is seminal to develop new technological devices. The study of those modifications or new phenomena releases a vast set of possibilities to include those structured materials in the construction of devices which exploit the quantum phenomena. Nevertheless, innovation can be generated by controlling some factors which are still associated to the bulk materials, as is the case of the antisite order. Among the multiple examples of these materials, the double perovskite Sr_2FeMoO_6 exhibits a considerable potential to be included in the development of spintronic devices, because it is a half-metallic ferromagnetic oxide with a high spin polarization. In addition to those characteristic properties, the Fe–Mo perovskite compound has a high Curie temperature which broads the potential applications of this material, including the development of devices to store information increasing his density [1].

In these kind of structures, the effect of the mis-site is important to understand the magnetic behavior. Based on the Sr_2FeMoO_6 compound, the structures $Sr_2Fe_{1+x}Mo_{1-x}O_6$ were studied through the mis-site disorder; changing the iron and molybdenum atoms ratio, the electric and magnetic properties of the material were studied. They must behave differently, due to the interaction among the magnetic moments, when the spatial distribution of the different atomic species changes. Being Sr_2FeMoO_6 between the single perovskites $SrFeO_3$ and $SrMoO_3$, the compounds generated by mis-site disorder must exhibit magnetic behaviors from ferromagnetism to antiferromagnetism and an effect on the half-metallicity which is characteristic of the double perovskite Sr_2FeMoO_6 [2].

2. Model and computational methods

A tetragonal cell was built using the reported data for bulk Sr_2FeMoO_6 double perovskite [3–7] (with the space group I4/mmm and lattice parameters $a = 5.5704$ Å and $c = 7.8983$ Å [7]). Then a supercell was constructed, connecting two conventional unit cells along the c axis, to study different compositions in the double perovskite $Sr_2Fe_{1+x}Mo_{1-x}O_6$; such supercell allows to change the Fe/Mo ratio. Along the [001] direction of the stoichiometric compound there are chains of atoms where Fe, O and Mo alternate orderly. From this periodic model, it has replaced Fe by Mo atoms and vice versa to model the anti-site disorder. Every atom replacement was made at the central chain of the supercell (Fig. 1) and the resulting arrangement is referred without mentioning the O atoms, because they are always between each pair of metals (Fe, Mo); even more, both metallic atom symbols were contracted to F and M for Fe and Mo, respectively.

Using the Materials Studio (MS) software [8], we performed single-point energy calculations using the DMol^3 module in the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional [9] and fine-accuracy options for all runs. We studied
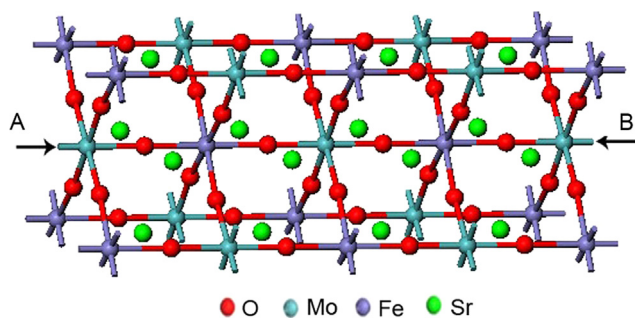
* Corresponding autor. Tel.: +52 5556242000.
E-mail address: ecarvajalq@ipn.mx (E. Carvajal).

the electronic properties of the bulk stoichiometric double perovskite and their variations on the basis of their density of states (DOS), by analyzing the molecular orbital composition based on the atomic orbital nature of the energy levels in isolated Fe, Mo, and O atoms and the atomic magnetic moments.

3. Results and discussion

The reference compound for this work is the Sr_2FeMoO_6; because of that, the study includes the density of states for the $Sr_2Fe_{1+x}Mo_{1-x}O_6$ compounds and the evolution of those DOS when the Fe/Mo concentration was modified in the double perovskite supercell. As discussed in Fig. 1, stoichiometric modifications are made by means of atomic substitutions along the A–B central chain (Fig. 1). These changes lead to both: loosing of the half-metallicity and modifications on the DOS symmetry, respect to the spin channels (Fig. 2). By including an iron atom ($x=0.25$) the half-metallic behavior remains, but shrinks the energy gap to around 0.2 eV for the up-spin channel, having a value of above 1 eV when the Fe:Mo content is 1:1 [10]. In contrast, when the chain A–B is composed just by Fe atoms ($x=0.50$), the Fermi level goes across a band flanked by two small energy gaps, for the up-spin channel.

It was assumed that mis-site disorder generates Fe–O–Fe chains in the $Sr_2Fe_{1+x}Mo_{1-x}O_6$ compounds [11], where Fe atoms are coupled antiferromagnetically. Our results agree with the scenario described by Topwal et al. (i)Increasing the number of Fe atoms in

such chains generated by the compound Fe enrichment ($x > 0$), the system starts loosing the spin polarization (Fig. 2) preserving a metallic ground state. As in the bulk material, the same critical impact on magnetization, of Fe/Mo ordering, was found for epitaxial Sr_2FeMoO_6 films [12].

Along the central chain of atoms, associated to an iron rich compound ($x > 0$), the Fe atoms are antiferromagnetically coupled, while the remaining Fe atoms couple ferromagnetically (Fig. 3). The presence of such Fe–O–Fe bonds reflects on the O behavior, it has a significant spin value along the direction where Fe atoms are antiferromagnetically coupled; on the perpendicular directions the spin values are about 30% lower, and this happens just at the neighbors of the central chain. In contrast what it was proposed for other perovskites, as in [13], previous results of calculations on single octahedral clusters excised from the bulk Sr_2FeMoO_6 [10] shown that neither t_{2g} nor e_g states is at the Fermi level; even more, the splitting suffered by those states is, at least, of a magnitude similar to the associated to the crystal-field splitting.

4. Conclusions

We investigated the local spin values for the double perovskites $Sr_2Fe_{1+x}Mo_{1-x}O_6$, in the range $-0.5 \leq x \leq 0.5$, founding that the greater the concentration of Fe atoms the compound is more clearly a metal where these atoms are coupled antiferromagnetically and this Fe richness affects the O behavior. Also, Fe deficiency

Fig. 1. Model supercell built up by connecting two conventional unit cells of the Sr_2FeMoO_6 along the c axis; as a result, the supercell contains four formula units. For the stoichiometric compound the central chain is referred as MFMFM, as described in the text. The Sr, Fe, Mo and O atoms are represented by the green, purple, blue and red spheres, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
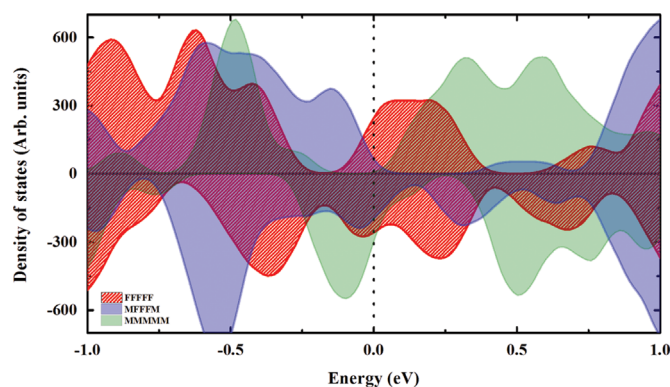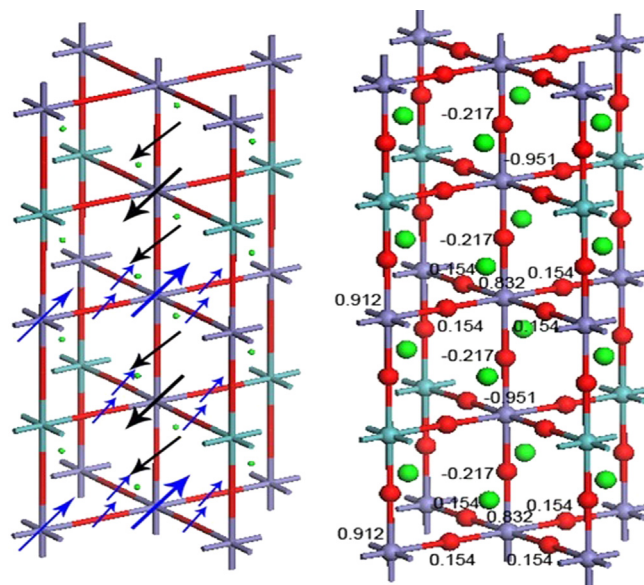

Fig. 2. Density of states, for the up-spin and down-spin channels (green arrows), for the modeled double perovskite supercells. The central chain configuration was tagged with the metal acronyms sequence and the corresponding color. The Fermi level is indicated by a vertical black dashed line. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Schematic spin values for the $Sr_2Fe_{1+x}Mo_{1-x}O_6$ compound, when $x=0.50$. Different color arrows correspond to different spin signs, while differences on size are associated to the respective spin values. Excepting the central chain, Fe atoms behavior is similar at all lateral chains.

Table 1

Iron percentage in each modeled double perovskite, with formula $Sr_2Fe_{1+x}Mo_{1-x}O_6$. Different compositions were generated by replacing Fe with Mo atoms along the chain tagged as A–B (Fig. 1); the resulting sequences, omitting the O atoms, are represented using F and M for iron and molybdenum, respectively.

Supercell central chain	x value in $Sr_2Fe_{1+x}Mo_{1-x}O_6$	Fe relative richness (%)
MMMMM	-0.50	-200
MMMFM	-0.25	-66.6
MFMFM	0.000	0.0
MFFFM	0.25	66.6
FFFFF	0.50	200

Table 2
Local spin values for the different supercell configurations. Each column tagged as lateral refers to the four equivalent atomic sequences along [001], except the one marked as central (A–B), as shown in Fig. 1.

Lateral		Central		Lateral		Central		Lateral		Central	
[001]	Spin value	[001]	Spin value	[001]	Spin value	[001]	Spin value	[001]	Spin value	[001]	Spin value
F	0.912	F	0.832	F	−0.168	M	0.043	F	0.235	M	0.338
M	0.021	F	−0.951	M	0.017	F	−0.226	M	0.290	M	0.822
F	0.912	F	0.832	F	0.936	F	1.117	F	0.235	M	0.338
M	0.021	F	−0.951	M	0.017	F	−0.226	M	0.290	M	0.822
F	0.912	F	0.832	F	−0.168	M	0.043	F	0.235	M	0.338

traduces in the loose of the half-metallic character, which remains for the moderate concentration of Fe atoms at the central chain of the model supercell. Tables 1 and 2.

Acknowledgments

References

[1] K.-I. Kobayashi, T. Kimura, H. Sawada, K. Terakura, Y. Tokura, Nature 395 (1998) 677–680.
[2] B. Aguilar, O. Navarro, and M. Avignon, Europhys. Lett. 88 (2009) 67003.
[3] B. García-Landa, C. Ritter, M.R. Ibarra, J. Blasco, P.A. Algarabel, R. Mahendiran, J. García, Sol. St. Commun. 110 (1999) 435–438.
[4] Y. Tomioka, T. Okuda, Y. Okimoto, R. Kumai, K.-I. Kobayashi, Y. Tokura, Phys. Rev. B 61 (2000) 422–427.
[5] A. Arulraj, K. Ramesha, J. Gopalakrishnan, C.N. R. Rao, Sol. St. Chem. 155 (2000) 233–237.
[6] J.B. Shi, Y.Y. Fan, P.H. Peng, F.C. Jou, C.Y. Lee, H.C. Ku, S.L. Young, H.Z. Chen, Physica B 329–333 (2003) 805–806.
[7] Q. Zhang, G.H. Rao, Y.G. Xiao, H.Z. Dong, G.Y. Liu, Y. Zhang, J.K. Liang, Physica B 381 (2006) 233–238.
[8] B. Delley, J. Chem. Phys. 113 (2000) 7756–7764.
[9] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865–3868.
[10] E. Carvajal, R. Oviedo-Roa, M. Cruz-Irisson, O. Navarro, Mater. Sci. Eng. B 177 (16) (2012) 1514–1517.
[11] D. Topwal, D.D. Sarma, H. Kato, Y. Tokura, M. Avignon, Phys. Rev. B 73 (2006) 094419.
[12] A.J. Hauser, R.E. Williams, R.A. Ricciardo, A. Genc, M. Dixit, J.M. Lucy, P.M. Woodward, H.L. Fraser, F. Yang, Phys. Rev. B (2011) 014407.
[13] B.C. Jeon, C.H. Kim, S.J. Moon, W.S. Choi, H. Jeong, Y.S. Lee, J. Yu, C.J. Won, J.H. Jung, H. Nur, T.W. Noh, J. Phys.: Condens. Matter (2010) 345602.