Electronic Properties and Magnetic Moment Distribution on Perovskite Type Slabs: Sr_2FeMoO_6, $SrFeO_3$ and $SrMoO_3$

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Abstract

Perovskite type slabs were excised from the Sr_2FeMoO_6, $SrFeO_3$ and $SrMoO_3$ bulk double perovskites, respectively, leaving (001) free surfaces. Supercells were built up for each slab, keeping a 10Å initial free space, to optimize the geometry. Once the minimum energy state was identified, the electronic and magnetic properties of the [001] oriented slabs have been calculated within the Density Functional Theory (DFT) scheme, with the Hubbard-corrected Local Density Approximation (LDA+U) and the CA–PZ functional. Magnetic moment for each atom in the systems was calculated; spin values for the Mo atoms are −0.02ħ, −0.13ħ and 0.56ħ for the $SrMoO_3$ slab system case and they are aligned antiferromagnetically. Contrarily, Mo magnetic moments in the Sr_2FeMoO_3 slab system align antiferromagnetically to the corresponding Fe atoms, being around 10% in magnitude; meanwhile, Fe moments increase and align ferromagnetically in $SrFeO_3$. The Densities of States (DOS) and band structures were calculated also to study the electronic behaviors. The vacuum region changes from the initial 10Å, as geometry stabilizes for all the slab cases; however, slab images separation evolves notoriously different for each model.

*Keywords:* Perovskite type slab, magnetic moment, density of states.

1 Introduction

Materials which have magnetic properties are very important because they are potentially useful to build up the novel generation of spintronic devices [1, 2]. At least as successors of manganite materials, some perovskites notoriously enhance the magnetoresistive ratio, turning into strong candidates to be incorporated in the design of information storage or spin filter devices. Among those

materials foreground some whose electric behavior made them half-metallic; such spin differentiation would permit to implement new features in the electronic devices, combining electronic, magnetic and even optical properties. Among the double perovskite materials, Sr_2FeMoO_6 distinguishes by their enormous magnetoresistance, ferromagnetic behavior and high Curie temperature [3]. Being highly sensitive to the Fe/Mo ratio content or antisite occupation, that compound will be more useful in the development of spintronics devices if it is nanostructured along specific crystalline orientations with precise free surfaces.

2 Model and computational method

From the Sr_2FeMoO_6 crystalline double perovskite (space group I4/mmm and lattice parameters a = 5.5704 Å and c = 3.9400 Å) a slab was excised to form a supercell, keeping 10Å of free space as initial separation between equivalent structures along the [001] direction; the same procedure was followed to construct slabs from the simple crystalline perovskites $SrFeO_3$ and $SrMoO_3$, having as reference [4]. The geometry of the perovskite type slabs was optimized in the Density Functional Theory scheme, by searching the minimum energy configuration, using the Hubbard−corrected Local Density Approximation (LDA+U) and the CA−PZ functional, as implemented in the CASTEP code.
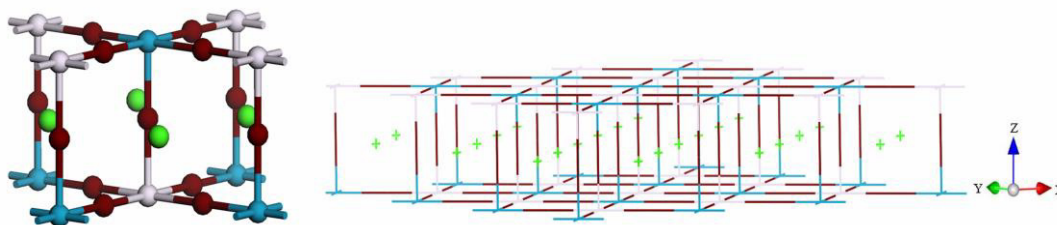
Figure 1: The Sr_2FeMoO_6 double perovskite type slab was excised from the crystalline material (space group I4/mmm and lattice parameters a = 5.5704 Å and c = 3.9400 Å.); the free surface is parallel to the (001) crystal plane and the shown views are the unit cell (left) and the slab (right). Red, blue, green and purple spheres (or sticks) represent O, Mo, Sr and Fe atoms, respectively (going from darker to lighter). For the $SrFeO_3$ and $SrMoO_3$ simple perovskites, the transition metal atoms are all Fe or Mo, respectively, in each unit cell.

3 Results and discussion

To keep half the high of the conventional cell, along the c base vector, diminish the calculation cost without information loses, because the upper and lower slab free surfaces are equivalent. The backup for this first assumption are the obtained parameter values (Table 1) for the Fe/Mo slab. Even more, the electronic behavior which characterizes the bulk material was retained by this slab: it is a half-metallic material; perhaps must be emphasized the fact that the energy band gap grows respect to the bulk value (Fig. 2). On the contrary, for the slabs generated from the simple Fe or Mo perovskites, the occupied electronic states led to conductor behavior in both cases (Figs. 3–4). The Mo perovskite case clearly shows the mentioned situation but the Fe case seems like the confinement induces the occupation of down−spin states in a small band, just to overcome the little gap between this and a bigger band of electronic states.

For each systems were calculated the atomic magnetic moments. Fe atoms in the $SrFeO_3$ slab have associated equally oriented moments which magnitudes are comparable. Meanwhile, magnetic moments of the metallic atoms in the $SrMoO_3$ slab differ in magnitude and are opposite oriented. That is, the Sr_2FeMoO_6, $SrFeO_3$ and $SrMoO_3$ slabs are ferri−, ferro−, and antiferromagnetic respectively; besides, interactions among transition metal atoms and O and Sr cause the appearance of little magnetic moments on these atoms, affecting the global magnetic behavior.

Perovskite system	Cell parameter $a = b$ (Å)	Cell parameter c (Å)	Cell parameter $a_1 = b_1$ (Å)	Cell parameter c_1 (Å)	Energy (eV)
Sr_2FeMoO_6	5.57	3.94	5.24	4.08	−11622.61
$SrFeO_3$	5.57	3.94	5.22	3.73	−830332.39
$SrMoO_3$	5.57	3.94	5.53	3.79	−13783.56

Table 1: Cell parameter values before (a, c) and after (a_1, c_1) calculations for geometry optimization. Energies for the optimized systems are shown on the column at the right.

The first remarkable result is linked to the slab which contains Fe and Mo. Reinforcing the initial postulation that having a slab with a thick of half **c** must be representative and enough for calculations (where the computational demand can be reduced), the magnetic moment distribution found for the lower energy configuration is the same at each free surface. Fe and Mo magnetic moments are coupled in an antiparallel way over each surface (Fig. 5); but individually, atoms of each kind of transition metal couple ferromagnetically. As would be expected, the Fe magnetic moment has the greater value and induces the corresponding moments on the other atoms; however, the latter are 10% (Mo) or 1% (Sr and O) of the former (Table 2).
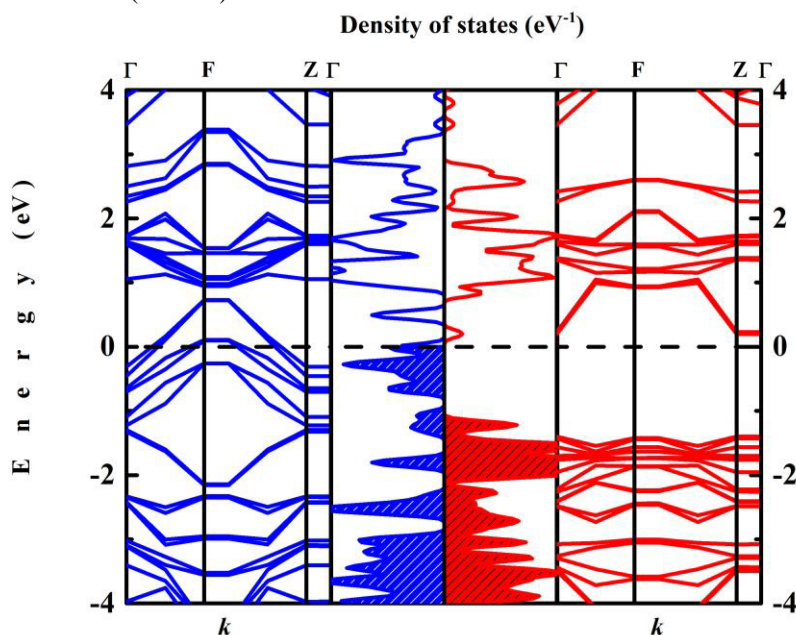
Figure 2: Bands structure and electronic density of states for the Sr_2FeMoO_6 double perovskite type slab. Graphs in blue (two at the left) correspond to the down−spin channel while graphs in red (two at the right) correspond to the up−spin channel. The black horizontal discontinuous line indicates the Fermi level and the central filled graphs indicate the occupied states.

Density of states (eV⁻¹)
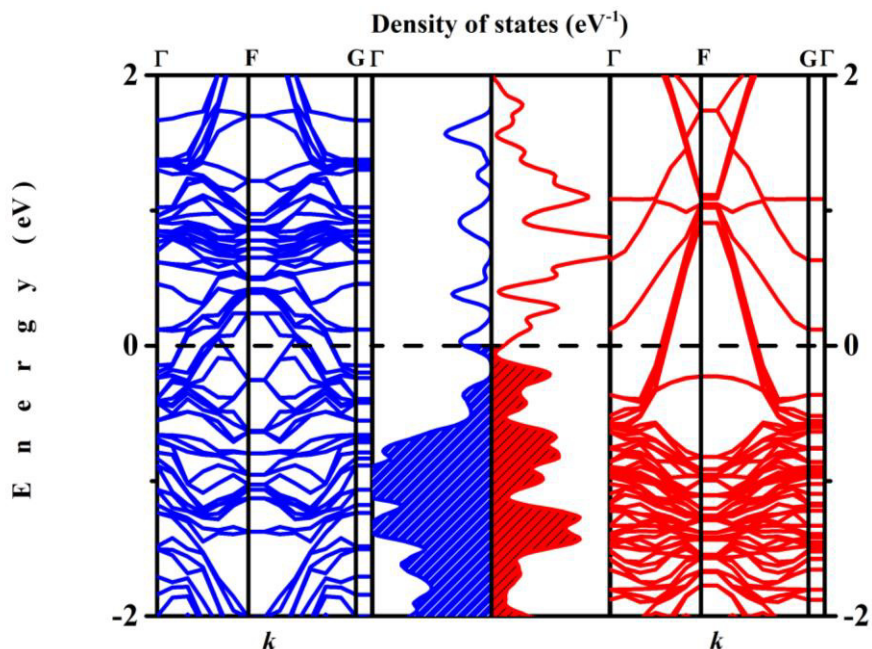
Figure 3: Bands structure and electronic density of states for the $SrFeO_3$ perovskite type slab. Graphs in blue (two at the left) correspond to the down–spin channel while graphs in red (two at the right) correspond to the up–spin channel. The black horizontal discontinuous line indicates the Fermi level and the central filled graphs indicate the occupied states.

Density of states (eV⁻¹)
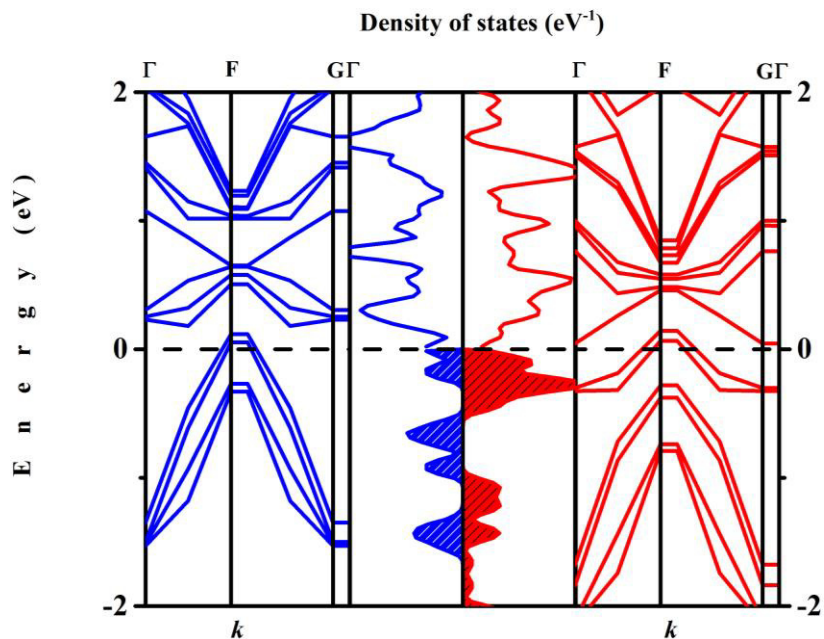
Figure 4: Bands structure and electronic density of states for the $SrMoO_3$ perovskite type slab. Graphs in blue (two at the left) correspond to the down–spin channel while graphs in red (two at the right) correspond to the

up–spin channel. The black horizontal discontinuous line indicates the Fermi level and the central filled graphs indicate the occupied states.

For the $SrFeO_3$ perovskite slab case each of the three atomic species adopt two possible values for the magnetic moment. Although all of them are ferromagnetically aligned, the O stand out over the other two because of the difference among their possible values. The greater magnetic moment values induced on the O atoms must be expected, because of the smaller separation between Fe atoms, which are their first neighbors. On the other hand, O and Mo behave in a similar way when this couple constitutes the $SrMoO_3$ perovskite type slab, both of these atoms have two possible magnetic moment values organized in an antiferromagnetic way. The present moments for this system do not induce any on the Sr atoms.

As it has been reported [5, 6], sensitivity and instability become critical because magnetoresistance diminishes, the structure must be keep by using a substrate and the expected bulk magnetization ($4\mu_B$/formula unit) falls and depends on the B-site order and the support temperature. Better values achieved for the saturated magnetization just reach $3\mu_B$ by formula unit [7].
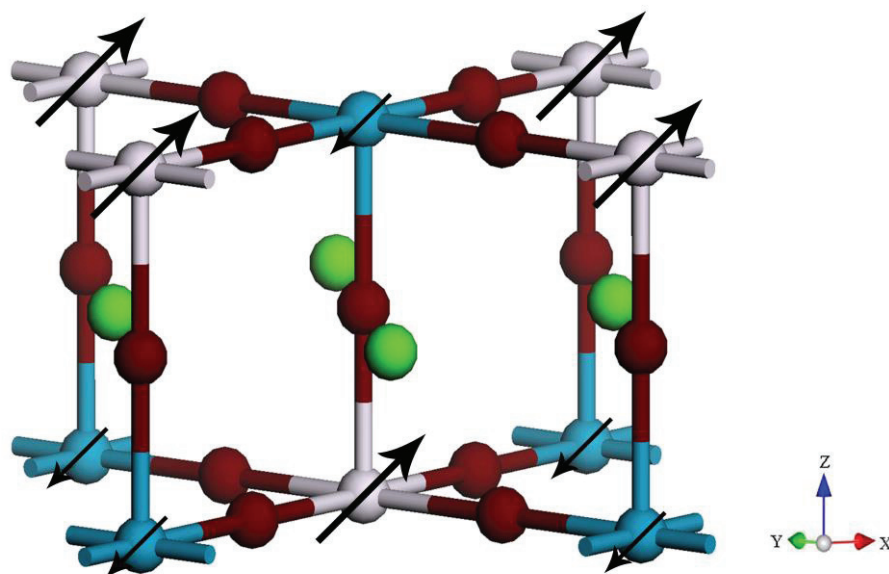
Figure 5: Distribution of the atomic magnetic moments (canted arrows above the atomic species) in the Sr_2FeMoO_6 slab. Red, blue, green and purple spheres (or sticks) represent O, Mo, Sr and Fe atoms, respectively (going from darker to lighter).

Perovskite system	Fe spin (ħ)	Mo spin (ħ)	O spin (ħ)	Sr spin (ħ)
Sr_2FeMoO_6	1.07	−0.13	0.01, 0.02	−0.01
$SrFeO_3$	2.49, 2.94		0.19, 0.44	0.02, 0.03
$SrMoO_3$		−0.02, 0.56	−0.01, 0.07	0.00

Table 2: Magnetic moment magnitude for the atoms in the different perovskite type slabs. The minus sign is to indicate the relative moment orientation corresponding to the different species. Some values appear individually (for Fe, Mo and Sr) because there is no variation related to each occupied site.

4 Conclusions

We have calculated the minimal energy structures for three slabs associated with bulk perovskite compounds. Furthermore, electronic densities of states, band structures and magnetic moment distributions were calculated, showing the strong dependence of the electronic and magnetic properties of these kind of confined systems on the transition metal species in the slab. The structure with the Fe/Mo content ratio equal to one still being a half metallic material, even with a different energy band gap value. The other two systems lose that character and turn to be metals, being especially notable for the Mo slab because the related bulk material is an insulator. Finally, must be noteworthy the effect of the transition metals on the O and Sr, affecting the whole magnetic behavior of each system.

5 Acknowledgments

References

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