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First principles study of the effects of disorder in the Sr_2FeMoO_6 perovskite

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First principles calculations were done in the double perovskite Sr_2FeMoO_6 regarding the effects of cationic disorder and electronic correlation in the ground-state properties such as spin polarization and magnetic saturation. We used the Generalized Gradient Approximation (GGA) method including a U Hubbard term. Results with 25% of disorder, where Fe-O-Fe and Mo-O-Mo configurations frequently occur, are shown. We found that disorder breaks down the half-metallic ferromagnetic behavior. We also calculated a magnetic saturation decrease from 4.0μ_B per formula unit to 2.22μ_B in accord with neutron magnetic scattering experiments.

Keywords: Double perovskite; cationic disorder; electronic correlation; half-metal compound.

PACS: 71.15.-m; 71.20.-b; 72.25.Ba; 85.75.-d

1. Introduction

Magnetic materials research has taken brand new directions with the increasing ability to synthetize materials whose charge carriers show an important spin-polarization. Also, advances in the field of electronics upon miniaturizacion of devices has served to expose spin-polarization effects. Should the development of fully spin-polarized materials succeed, then the field of spintronics would boost the electronic industry with much smaller and robust devices with intrinsic memory. In these sense halfmetallic ferromagnetic oxides have attracted extensive attention not only as a source of fully spinpolarized charge carriers for spintronic applications, but also as potential candidates for magnetoelectronic elements by virtue of their colossal magnetoresistance [1, 2]. In 1998 K. -I. Kobayashi *et al*. [2], reported a large magnetoresistance effect with a fairly high magnetic transition temperature of about 418 K in Sr_2FeMoO_6 (SFMO), a material belonging to the class of double perovskites (ABB'O_6), where the alkaline-earth ion A is Sr and transition-metal ions B and B' are Fe and Mo arranged in a rock-salt structure, respectively [3].

Despite many theoretical studies, a thorough comprehension of the electronic and magnetic properties of such system is not been achieved. It is known that changes in the composition of the SFMO compound modify radically its physical properties, as well as anti-sites defects do [4, 5]. The experimental value of the saturation magnetization (M_S) is invariably found to be lower than the expected value of 4.0μ_B per formula unit (f.u.). This is due to the inevitable presence of mis-site disorder, where some Fe and Mo interchange their crystallographic positions. However, the microscopic origin of the M_S decrease is still not entirely clear. Both classical Monte Carlo simulations [6] and quantum-mechanical band structure [3] indeed predicted a reduction of M_S as a function of mis-site disorder, but the underlying reason for this reduction is very different in these two approaches. In the first one [6], it is assumed that M_S decreases due only to anti-ferromagnetically coupled Fe pairs whenever Fe-O-Fe bonds are generated by such mis-site disorders. According to this, the conduction band presumably retains its polarization to a large extent. In contrast, the second approach [3] attributes the decrease of M_S to strong depolarization effects at each site, though all Fe sites were found to be ferromagnetically coupled. On the other hand, experimental results from neutron magnetic scattering [7] in samples with nominally ordering of $\sim$ 70% and $\sim$ 18% nominally disordered, suggest that the diminished value of M_S originates upon naturally occurring groups of Fe cations in which strong anti-ferromagnetic (AFM) Fe-O-Fe super-exchange interactions are promoted, similar to those in the $LaFeO_3$ perovskite. These Fe groups are not magnetically isolated, but coupled by virtue of Fe-O-Mo AFM interactions, which maintain the long-range coherence of this AFM structure [7]. In this paper, we propose a correlated picture to investigate the effect of cationic disorder on the electronic and magnetic properties of the double perovskite SFMO by a structural optimization and use of first principles calculations within the generalized gradient approximation (GGA) with an effective on-site correlation in Fe and Mo sites. The optimized structure with lower energy is used to calculate the density of states (DOS) in each case.

2. Method

The double perovskite SFMO is a body-centered tetragonal structure, with a space group I4/mmm and lattice parameters $a = b = 5.57$ Å and $c = 7.90$ Å [2]. The FeO_6 and MoO_6

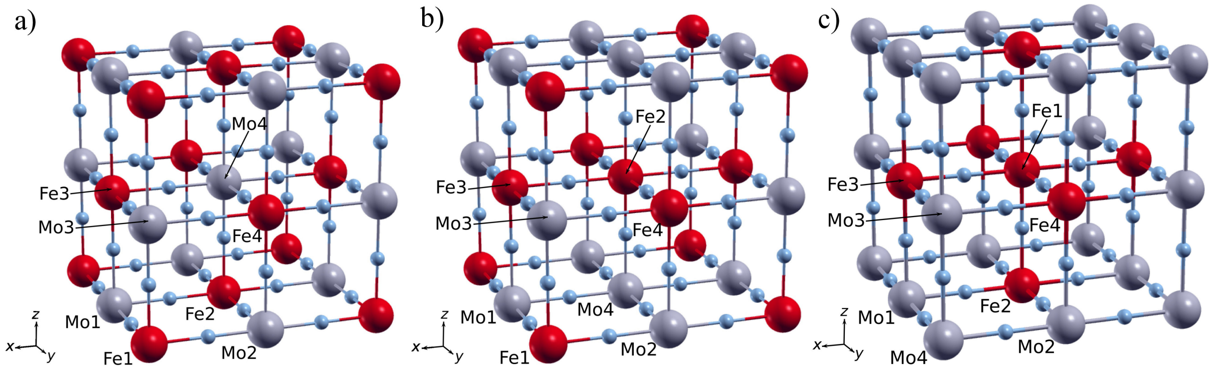

FIGURE 1. (Color online) Crystal structure of four atomic formulas of the ordered and disordered structures of SMFO. Disordered structures are shown for two different anti-sites. a) Ordered SMFO structure. b) First anti-site configuration, Mo4 and Fe2 are interchanged, while in c), the second anti-site configuration, Mo4 and Fe1 have been interchanged. The space group is I4/mmm [2], with Fe atoms (red) and Mo (gray tones) atomic sites alternated with O (blue). Into each cubic sub-cell there is a Sr atom.

in octahedral configuration are alternately organized along the cubic three axes, whereas the Sr atoms are located body-centered into the structure [2]. In Fig. 1, we show a supercell formed by four structures per unitary formula. In order to simplify the view only sites occupied with Fe, Mo and O atoms are shown.

Calculations were performed with the QUANTUM ESPRESSO package [8] employing density functional theory and the Perdew-Burke-Ernzerhoff exchange-correlation functionals [9]. The ultrasoft pseudopotentials RRKJ [10] in the ion-electron interaction were used for the Fe 3d, Mo 4d, O 2p ions and the VAN pseudopotentials [11] for the Sr 5s, with semicore electrons included in the valence, as well as a plane-wave basis set for electronic wave functions and the charge density, with energy cutoffs of 50 and 200 Ry, respectively. The structural optimizations were calculated with quasi-Newton BFGS preconditioning [8]. The electronic Brillouin zone integration in the self-consistent calculation was found to converge with a $6 \times 6 \times 6$ uniform k-point mesh. The density of states calculation was sampled with $12 \times 12 \times 12$ uniform k-point mesh and a gaussian smearing of 0.02 Ry. We used GGA+U approximation, which allowed us to obtain a correct magnetic ground state for SFMO. An effective exchange correlation was set on Fe and Mo of 3 eV and 1 eV, respectively [12]. Disordered configurations of the SFMO system were simulated upon introduction of anti-sites, *i.e.*, Fe and Mo sites were interchanged. We also tested the case of parallel and anti-parallel spin polarization on the Fe anti-sites (Figs. 1b and 1c).

In order to compare the electronic structures of the ordered and disordered SFMO on the same footing, calculations were performed by constructing supercells of four formula units, giving a 75% order and 25% disorder, in agreement with experimental results by D. Sánchez *et al.* [7] who obtained structures at 15 K with $\sim$ 68% order and $\sim$ 18% disorder. Fe ions were placed in the following sites: Fe1(0, 0, 0), Fe2(0.5, 0.5, 0), Fe3(0.5, 0, 0.5), Fe4(0, 0.5, 0.5) and Mo ions were placed in: Mo1(0.5, 0, 0), Mo2(0, 0.5, 0), Mo3(0, 0, 0.5), Mo4(0.5, 0.5, 0.5) as shown in Fig. 1a). The effect of positional disorder at Fe/Mo sites is simulated by interchanging Fe and Mo sites, so as to generate different physical environments surrounding each inequivalent Fe and Mo sites. We have performed the disordered calculation for two different disordered configurations, looking for the most probable one comparing their total energies of the cell variable ground-state structure optimization calculations. The first configuration is obtained by interchanging the Fe2 and Mo4 sites, *i.e.*, nearest-neighbor Fe-Mo ions were switched. For the second configuration the Fe1 and Mo4 ions, corresponding to second nearest-neighbor, were interchanged. Figures 1b and 1c show the corresponding structures with an interchange of only one Fe-Mo pair. The structure shown in Fig. 1b can be derived from the structure shown in Fig. 1a by replacing the body centered Mo with the face-centered Fe sites in xy plane. Similarly, the structure in Fig. 1c is derived by replacing the body centered Mo with the Fe placed at the corners. These replacements in turn lead to the distribution of inequivalent Fe and Mo sites [3].

3. Results and discussion

The first disordered configuration with anti-ferromagnetic spin orientation, shown in Fig. 1b, has a minimal total energy of -7378.781 eV corresponding to the most probable disordered configuration. This crystalline structure has lattice parameters $a = b = 5.57$ Å and $c = 7.69$ Å. We can see from Fig. 1a that the interchange of Fe2 and Mo4 atoms let the Fe2 atom in the middle of a Mo-Fe-Mo chain, where Fe2 has 4 Fe in the xy plane as nearest-neighbors. In the first disordered AFM configuration (Fig. 1b), the local magnetic moment of Fe2 and Mo4 anti-sites is $-3.59\mu_B$ and $0.17\mu_B$, respectively. The total magnetic moment of the system is $2.22\mu_B$ in agreement with experimental results [7]. In the second disordered AFM configuration (Fig. 1b), the local magnetic moment of Fe1 and Mo4 anti-sites is $-3.35\mu_B$ and $0.24\mu_B$, respectively. The total magnetic moment of the systems is $2.56\mu_B$. We

TABLE I. Distribution of Mo and Fe neighbors at various shells for inequivalent Fe and Mo sites for the ordered and two disordered structures. The last three columns show the magnetic moment at various inequivalent sites, total magnetic moment, total energies of the optimization calculations and, in parenthesis, total energy of self-consistent field calculation.

	Sites	Neighbors	Magnetic moment [μ_B/f.u.]	Total magn. moment [μ_B/f.u.]	Total energy per f.u. [eV]
Ordered	Fe	6 Mo	3.60	4.00	-7379.188
	Mo	6 Fe	-0.28		(-7376. 480)
First disordered configuration	Fe1	6 Mo	3.64	2.22	-7378.781
	Fe2	4 Fe + 2 Mo	-3.59		(-7376.413)
	Fe3,Fe4	2 Fe + 4 Mo	3.60		
	Mo1, Mo2	4 Fe + 2 Mo	-0.06		
	Mo3	2 Fe + 4 Mo	-0.25		
	Mo4	6 Fe	0.17		
Second disordered configuration	Fe1	6Fe	-3.35	2.56	-7378.708
	Fe2, Fe2, Fe4	2 Fe + 4 Mo	3.64		(-7376.403)
	Mo1, Mo2, Mo3	4 Fe + 2 Mo	0.05		
	Mo4	6Mo	0.24		

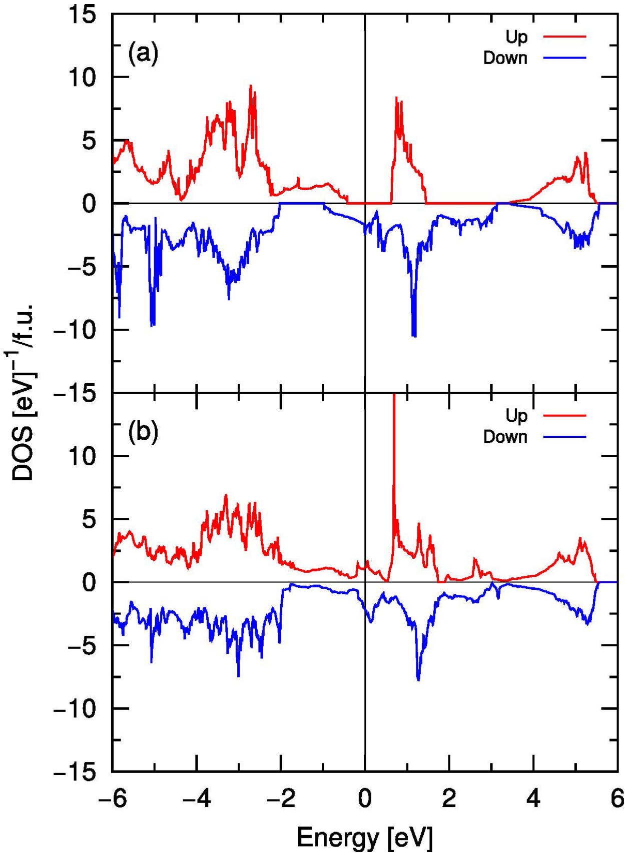

FIGURE 2. (Color online) Total electronic density of states (DOS) for: (a) Ordered double perovskite SFMO, (b) Disordered double perovskite SFMO. Each panel show the up-spin channel (red) and the down-spin channel (blue). The Fermi energy is set to zero.

also computed the FM cases for the two configurations and the total magnetic moment values were $3.87\mu_B$ and $4.25\mu_B$, respectively, far away from experimental results.

In the energy range shown in Fig. 2 the total electronic DOS is essentially determined by Fe 3d and Mo 5d orbitals. Figure 2a shows the total DOS for the ordered SFMO structure where the half-metallic behavior is observed and the up-spin channel has a gap of 1.06 eV, while the down-spin channel is present at the Fermi level. The total DOS for the first disordered SFMO structure with AFM coupling is shown in Fig. 2b, where the half-metallic feature is broken down in majority ($\sim 75\%$) by Mo 5d orbitals in the up-spin channel, showing the SFMO compound as a normal paramagnet, with states in both up and down-spin channels.

The ground-state magnetic structures for all studied disordered configurations were found to be at the AFM state. In our optimized cell structure we found that the first disordered configuration has the lower total energy, see Table I. Using the optimized ground-state structure cell we computed both the AFM and FM disordered configurations comparing their SCF total energies. Results show that the better configuration is the AFM one, in agreement with the Monte Carlo simulations [6], and magnetic scattering results [7].

In Table I, it can be observed that the magnetic moments at the Fe sites are strongly influenced by the number of the Mo atoms in the nearest-neighbor shell. The higher the number of Mo neighbors surrounding each Fe atom, the larger the magnetic moment. In the first AFM configuration the magnetic moment at Mo sites change from $-0.25\mu_B$ with 6 Fe nearest-neighbors to $0.17\mu_B$ with 2 Fe nearest-neighbors. This behavior may be explained because the Fe and Mo are anti-sites anti-ferromagnetically coupled, besides, the fact that both Fe/Mo have lower magnetic moment means that they are less correlated with respect to its neighbors making hopping between sites possible. In addition, our calculations of the total DOS for the AFM disordered configuration (Fig. 2b), show that the system loses its half-metallic character due to the super-exchange correlation in Mo chains, formed when the substitution is done by AFM Fe2. The spin-up states present in disordered configuration DOS are due to Fe2, which increases the probability of hopping from the Mo4 to the Fe2 site via Pauli exclusion principle, giving the possibility of only spin-up electrons jumping in the Mo-Fe-Mo chain or the Fe plane. We can also argue from Fig. 2b that the behavior of the up channel in the range from -0.15 eV to 0.06 eV corresponds to that of a Mo-Fe-Mo chain and the peak at 0.34 eV can be associated to a Mo plane.

4. Conclusions

Our ground-state structural optimization predicts that disorder may lead to AFM couplings between neighboring Fe sites, in agreement with Monte Carlo calculations [6] and neutron magnetic scattering experiments [7], instead of FM coupling proposed for the idealized structure [3]. The electronic structure shows a half-metal breakdown for a 25% disorder in the double perovskite SFMO due to the charge transfer from Mo to Mo-Fe-Mo chain with anti-ferromagnetically coupled Fe, increasing the spin-up states at the Fermi level and decreasing the theoretical saturation magnetization from $4.0\mu_B$ to $2.22\mu_B$, in agreement with experimental results [7].

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