Physics Letters A 379 (2015) 2897–2901

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

Vacancy-induced insulator – direct spin gapless semiconductor – half-metal transition in double perovskite La_2CrFeO_6: A first-principles study

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ARTICLE INFO

Article history:
Received 28 July 2015
Received in revised form 4 September 2015
Accepted 19 September 2015
Available online 25 September 2015
Communicated by R. Wu

Keywords:
La_2CrFeO_6
Structural property
Electronic structure

ABSTRACT

Double perovskite oxide La_2CrFeO_6 with the characteristic of ferrimagnetic insulator has been reported by Chakraverty and Lee et al. Engineering the physical properties of materials, including obtaining unusual properties, can be achieved by some measures, and defect-tuning has been one of the most efficient measures. Here, by using density-functional calculations, La vacancy is introduced in La_2CrFeO_6 and special properties are obtained successfully. The results show that the magnetic phase of La_2CrFeO_6 would transfer from ferrimagnetic to ferromagnetic ordering as long as La vacancy is introduced. Furthermore, $La_{1.75}CrFeO_6$ shows direct spin gapless semiconductor, and $La_{1.5}CrFeO_6$ behaves as half-metal with the half-metallic gap of 0.42 eV. In the whole range of La vacancy, the electronic configurations of both Cr and Fe ions exhibit high-spin states, the magnetic moment of Fe remains 4.20 μ_B, while that of Cr ions decreases from 2.66 to 1.97 μ_B with increasing the amount of La vacancy. This work opens an alternative way to design spintronic materials, especially for direct spin gapless semiconductors which have never been reported in perovskite oxides.

1. Introduction

Half-metals have been reported by de Groot et al. early in 1983 [1]. Since they simultaneously exhibit metallic and semiconducting characteristics in the two spin channels, half-metals have potential technological applications in spintronic field, such as single-spin electron source, high-efficiency magnetic sensors, etc. [2–5]. Therefore, half-metals have attracted enormous attention, and a lot of half-metallic materials have been reported both in experimental and theoretical methods, such as heusler alloys [1,6], zincblende structure compounds [7], chromium dioxide [8–10], magnetite [11–14], graphene [15,16], boron-nitride nanostructures [17,18], one-dimensional polymers [19], and so on.

Double perovskite oxides also have attracted a great interest due to their particular properties and simple structures, such as multiferroic [20]. Half-metallicity has been another highlighted property for double perovskite oxides since the experimental discovery of Sr_2FeMoO_6 in 1998 [21]. Thus, up to now, a great deal of interest has been implemented into searching for such materials with the chemical formula of $A_2BB'O_6$. Besides their simple structures, possessing high Curie temperature (T_c) is another superiority of some reported double perovskite oxides over other types of half-metals [21–23]. The high T_c is one important factor of half-metals, because only the half-metals with high T_c can work at room temperature [24,25]. Besides high T_c, large half-metallic gap, defined as the minimal energy gap for a spin excitation, is also essential for half-metals to be practically applied in spintronic field, because the large half-metallic gap can efficiently prevent the spin-flip transition of electrons caused by thermal excitation and preserve half-metallicity at room temperature.

Unfortunately, although some half-metals have been predicted theoretically, very few half-metals have been successfully synthesized by experiment. The main reason is that the most theoretically reported half-metals are in stoichiometric form, while the defect is experimentally inevitable and will usually change the band structure of the compounds. However, for Sr_2FeMoO_6, the half-metallic characteristic is preserved even with existent of vacancy, as previously reported [26]. Perhaps this is another reason of being the hot half-metallic material for double perovskite oxide Sr_2FeMoO_6. Therefore, searching for various half-metals is extremely important to solve these inevitable limitations and obtain suitable materials on the corresponding practical applications.

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http://dx.doi.org/10.1016/j.physleta.2015.09.028
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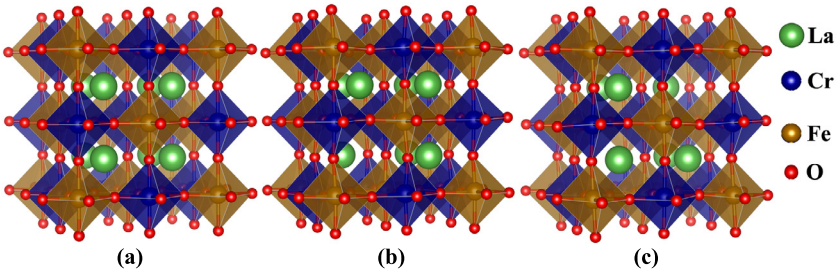

Fig. 1. (Color online.) The optimized structures of the ground-state $La_{2-x}CrFeO_6$. (a), (b), and (c) are for $x = 0$, 0.25, and 0.5, respectively.

Based on this fact, tuning the existing materials into half-metals by changing the external environment or internal chemical environment is more reasonable and practicable.

La_2CrFeO_6 (LCFO) has been experimentally synthesized by Chakraverty in 2011 and shows well-ordering on the transition-metal sites [27]. In 2012, Lee et al. studied the electronic property of LCFO by first-principles study, and the result shows LCFO behaves as an insulating ferrimagnet [28]. This result is in good agreement with the experimental data reported by Chakraverty et al. [27], but it is contrary to the other theoretical calculations which tells it exhibits half-metallic ferrimagnet or insulating ferromagnet [29,30]. This contradiction drives us to do further study on the property of LCFO, and our calculational result shows that the ground-state LCFO behaves as ferrimagnetic insulator with different band gap in the two spin channels, and this is consistent with both the experimental and theoretical datas given by Chakraverty et al. [27]. Mentionably, it is practicable to transfer the material from ferrimagnetic insulator to magnetic half-metal via some control measures, such as defect doping which can be achieved in experiment. For instance, in single-layered manganese dioxide nanosheets with ferromagnetic semiconducting nature, half-metallic property was successfully engineered by introducing vacancy, as reported by Wang et al. [31].

The above information motivates us to further study and engineer the electronic property of LCFO by doping vacancy on La site in this work. As a result, the electronic property of LCFO is successfully tuned, and the direct spin gapless semiconducting and half-metallic characteristics are successionally presented with increasing the content of La vacancy. Remarkably, the direct spin gapless semiconductor, another important material in spintronic field, is never reported previously in perovskite oxides. This opens an alternative way to search such materials in perovskite oxides which is almost the most abundant mineral on the earth.

2. Computational methods

In this work, the underlying *ab initio* structural relaxations and electronic band structure calculations were carried out by using generalized-gradient approximation (GGA) plus a Hubbard U (on-site Coulomb repulsion) framework and the projector-augmented-wave (PAW) potentials as implemented in VASP [32,33]. The on-site Coulomb and exchange parameters were $U = 4.0$, $J = 1.0$ eV for Cr, and $U = 6.0$, $J = 1.0$ eV for Fe, chosen by the fact that the calculated structure with these parameters are in good agreement with the experimental data. The structural relaxations were performed until the Hellmann–Feynman force on each atom reduces by less than 0.001 eV/Å. To ensure high accuracy, the k-point density and the plane waves cutoff energy are increased until the change of the total energy was less than 10^{-5} eV, and finally the Brillouin-zone (BZ) integration is carried out using $12 \times 12 \times 12$ Monkhorst–Pack grid in the first BZ, the plane waves with the kinetic energy up to 550 eV is employed. In addition, the simulations were performed using a $2 \times 2 \times 2$ supercell based on ABO_3 cubic cell.

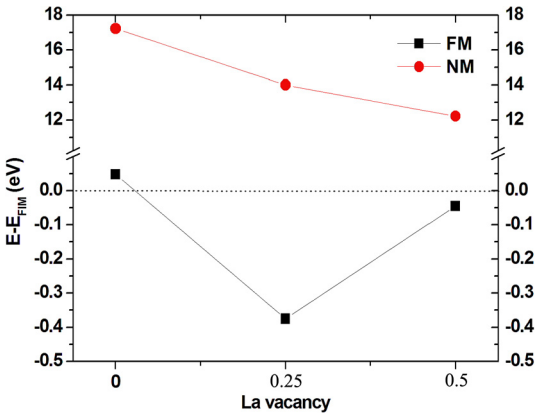

Fig. 2. (Color online.) The total energies of $La_{2-x}CrFeO_6$ with three different magnetic phases. All the values are relative to those of ferrimagnetic ones which are taken as zero.

Table 1
The parameter x is for the amount of La vacancy per formula. The parameter a is the lattice constant (in Å). The d_{Cr-O} and d_{Fe-O} (in Å) are the lengths of the Cr–O and Fe–O bonds, respectively. The A_{O-Cr-O}, A_{O-Fe-O}, and $A_{Fe-O-Cr}$ (in °) are the value for O–Cr–O, O–Fe–O, and Fe–O–Cr angles, respectively.

x	a	d_{Cr-O}	d_{Fe-O}	A_{O-Cr-O}	A_{O-Fe-O}	$A_{Fe-O-Cr}$
0	7.79	1.94	1.96	180	180	180
0.25	7.74	1.90/1.94	1.94/1.99	173	173	170
0.5	7.70	1.89	1.96	180	180	174

3. Results and discussion

3.1. The response properties of the ground-state LCFO

The properties of the ground-state LCFO are investigated firstly, and the optimized structure is pictured in Fig. 1(a). In order to reveal the magnetic ordering of LCFO, the three magnetic phases, ferromagnetic (FM, ferromagnetically coupled within each sublattice and between the two sublattices), ferrimagnetic (FIM, ferromagnetically coupled within each sublattice and antiferromagnetically coupled between the two sublattices), and nonmagnetic (NM) configurations, are employed here. The total energies of LCFO with the three phases are plotted in Fig. 2, and the result shows that the FIM one has the lowest total energy, at least 0.05 and 17.22 eV lower than those of the FM and NM ones, respectively. This fact indicates that the ground-state LCFO has FIM ordering, in agreement with the experimental result [27]. The optimized structure of the ground-state FIM LCFO shows the space group of $Fm\bar{3}m$ (No. 225), and some parameters are listed in Table 1. The lattice constant is 7.79 Å, and the lengths of Cr–O and Fe–O bonds are 1.94 and 1.96 Å, respectively. All the O–Cr–O, O–Fe–O, and Cr–O–Fe angles are 180°. These calculated results are consistent with those given by the experimental study [27].

The magnetic property is described in Fig. 3. The magnetic moments on Cr and Fe sites are 2.66 and −4.29 μ_B, respectively, and the net magnetic moment is −2.07 μ_B per formula unit, agreeing