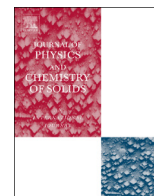




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journal homepage: www.elsevier.com/locate/jpcsFirst-principles investigations on electronic and thermodynamic properties of double perovskite Sr_2XMoO_6 ($\text{X}=\text{Ge}$ and Si)

Lei Li, Qiang Gao, Gang Lei, Huan-Huan Xie, Jian-Bo Deng, Xian-Ru Hu*

Department of Physics, Lanzhou University, Lanzhou 730000, People's Republic of China

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ABSTRACT

We present a study of the electronic and thermodynamic properties of Sr_2XMoO_6 ($\text{X}=\text{Ge}$ and Si) based on the density-functional theory first-principles calculations. It is found that $\text{Sr}_2\text{GeMoO}_6$ is a half-metallic ferromagnet and $\text{Sr}_2\text{SiMoO}_6$ is a metallic ferromagnet within the local spin density approximation (LSDA). But using a correlated band theory $\text{LSDA}+U$, the results indicate that both compounds are half-metallic ferromagnets with a total spin magnetic moment per formula unit of $2.00 \mu_B$. Through the analysis of crystal-field-splitting and spin-splitting, we find that the main magnetic moment contribution comes from the $\text{Mo}-t_{2g}$ states and $\text{O}-2p$ states for both compounds. Finally, by using a quasi-harmonic Debye model, the bulk modulus, heat capacity, Debye temperature and the coefficient of thermal expansion have also been obtained in the present work. The present calculations show that $\text{Sr}_2\text{GeMoO}_6$ and $\text{Sr}_2\text{SiMoO}_6$ may be promising materials for future spintronics applications.

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1. Introduction

Half-metallic ferromagnets (HMFs) have shown great potential in spintronic devices since its introduction by de Groot and his colleagues in the early 1980s [1]. Ideally, half-metals have the band structure, one of spin channel of which exhibits metallic behavior, while the other spin channel exists a gap at the Fermi level. Thus, the following three characteristic properties can be observed: (1) 100% spin polarization at the Fermi level (E_F); (2) quantization of magnetic moment; (3) zero spin susceptibility. Those properties offer opportunities for a new generation of devices combining standard microelectronics with spin-dependent effects such as nonvolatile magnetic random access memories and magnetic sensors [2]. Therefore, the search for half-metallic compounds is a highly popular topic, such as rutile CrO_2 [3], spinel Fe_3O_4 [4], Mn-doped GaAs [5,6] and double perovskites La_2VTcO_6 , La_2VCuO_6 [7].

Among half metals (HMs), the complex oxides with double perovskite (DP) structure $\text{A}_2\text{BB}'\text{O}_6$ have attracted much attention to researchers because a variety of options are available for substituting the A-site or B-site elements. On the B-site elements, transition metal ions are used as their diverse electronic configurations in d -orbitals. On the A-site elements, alkaline earth or rare-earth ions, such as Ca, Sr, Ba and La, are often used as HMs. In the past years DP compounds have been investigated widely and sufficiently. For example, DP Ba_2VTO_6 ($\text{T}=\text{Nb}$, Mo) [8] are not

HMFs within local spin density approximation (LSDA), but HMFs under $\text{LSDA}+U$ (considering the Coulomb correlations). DP $\text{La}_2\text{CrFeO}_6$ is predicted to be a HMF by both experiment [9] and density function theory (DFT) calculations [10]. A lot of Sr-based DP $\text{Sr}_2\text{BB}'\text{O}_6$ have been predicted to be HMs, such as $\text{Sr}_2\text{FeMoO}_6$ [11–14], $\text{Sr}_2\text{FeReO}_6$ [12,15], Sr_2FeWO_6 [13], Sr_2CrWO_6 [12,16], $\text{Sr}_2\text{CrMoO}_6$ [14], $\text{Sr}_2\text{GdReO}_6$ [17] and Sr_2ZnBO_6 ($\text{B}=\text{Tc}$, Re , Os , Pd and Au) [18].

With LSDA calculation, Kee reported DP $\text{Sr}_2\text{CrFeO}_6$ to be a simple metallic ferrimagnet [9]. However, considering Coulomb correlations, DP $\text{Sr}_2\text{CrFeO}_6$ is predicted to be a HM [10], which is also confirmed by fixed spin moment calculations. Hence, the Coulomb correlations may probably influence the DFT calculations of DP oxide when calculated compounds consist of transition metals.

Motivated by the above, we present a study on Sr-based DP compounds Sr_2XMoO_6 ($\text{X}=\text{Ge}$ and Si), which also consist of rare earth and transition metal element. In both compounds, up to now, no reports on the half-metallicity have been found. So, it is necessary to study systematically the electronic structure and magnetic properties of the Sr_2XMoO_6 ($\text{X}=\text{Ge}$ and Si) compounds by LSDA and $\text{LSDA}+U$ calculations. The present paper is organized as follows. In Section 3.1, we investigated the Sr_2XMoO_6 ($\text{X}=\text{Ge}$ and Si) using the LSDA method. Our results show that $\text{Sr}_2\text{GeMoO}_6$ is a HMF and $\text{Sr}_2\text{SiMoO}_6$ is a metallic ferromagnet. In Section 3.2, we perform the calculation using $\text{LSDA}+U$, and we find that both compounds are HMFs. In Section 3.3, some thermodynamic properties are presented and discussed. Finally, some conclusions are drawn in Section 4.

* Corresponding author.

E-mail address: huxianru@lzu.edu.cn (X.-R. Hu).

2. Structure and calculation method

In theory, the crystal structure of the double perovskite compounds Sr_2XMoO_6 ($\text{X}=\text{Ge}$ and Si) can be determined by the value of tolerance factor (t_f). t_f is defined by

$$t_f = \frac{r_{\text{Sr}} + r_{\text{O}}}{\sqrt{2} \left(\frac{r_{\text{B}} + r_{\text{Mo}}}{2} + r_{\text{O}} \right)}, \quad (1)$$

where r_{Sr} , r_{B} ($\text{B}=\text{Ge}$ and Si), r_{Mo} and r_{O} are the ionic radius of Sr, B, Mo and O atoms, respectively. t_f is obtained by using SPuDS (Structure Prediction Diagnostic Software) code [19,20]. We calculate the DP compounds by employing the formula $\text{A}_2\text{BB}'\text{O}_6$ of the NaCl B-cation ordered perovskite with space group of $\text{Fm}\bar{3}\text{m}$ (No. 225). In the cubic DP structure $t_f \approx 1$, when $t_f < 1$ the bond angle of superexchange $M-O-M'$ varies from the ideal, 180° . In consequence, the ideal cubic becomes rhombohedral or orthorhombic, and if $t_f > 1.05$, a hexagonal structure is formed [21]. The calculated tolerance factors t_f of $\text{Sr}_2\text{GeMoO}_6$ and $\text{Sr}_2\text{SiMoO}_6$ are 1.000 and 1.032, respectively. According to the value of t_f , both DP compounds are cubic crystal structure with space group $\text{Fm}\bar{3}\text{m}$ indeed. In addition, we can also calculate the lattice constants (a) and Wyckoff positions for DP compounds by using SPuDS. For $\text{Sr}_2\text{GeMoO}_6$, the lattice constant is 7.87 Å, and the Wyckoff positions of Sr, Ge, Mo and O are $8c(0.25, 0.25, 0.25)$, $4a(0, 0, 0)$, $4b(0.5, 0, 0)$ and $24e(0.2412, 0, 0)$, respectively. For $\text{Sr}_2\text{SiMoO}_6$, the lattice constant is 7.62 Å, and the Wyckoff positions of Sr, Si, Mo and O are $8c(0.25, 0.25, 0.25)$, $4a(0, 0, 0)$, $4b(0.5, 0, 0)$ and $24e(0.2328, 0, 0)$, respectively. So the following calculations are based on the obtained crystal structure information.

The present calculations are carried out with LSDA and LSDA+ U approaches implemented in the first-principles full-potential local-orbital (FPLO) minimum-basis method code [22,23]. The Perdew Wang 92 potential [24] is used for calculations. For the Brillouin zone integration, we use the k meshes of $20 \times 20 \times 20$ for all calculations. For a self-consistent field iteration, the convergence criterion is set to both the density (10^{-6} in code specific units) and the total energy (10^{-8} hartree).

3. Results and discussion

3.1. Local spin density approximation electronic structure

The LSDA total and atom-projected density of states (DOSs) of $\text{Sr}_2\text{GeMoO}_6$ and $\text{Sr}_2\text{SiMoO}_6$ at equilibrium lattice constants are shown in Fig. 1. For $\text{Sr}_2\text{GeMoO}_6$, the spin-up channel is metallic whereas in the spin-down channel there is an energy gap around the Fermi level of about 2.68 eV. Therefore, the compound is a HMF. The half metallic gap [25–27], which is determined as the minimum between the lowest energy of spin-up (-down) conduction bands with respect to the Fermi level and the absolute values of the highest energy of the spin-up (-down) valence bands, is 0.24 eV. But for $\text{Sr}_2\text{SiMoO}_6$, both the spin-up and spin-down electrons exhibit metallic character. So the compound is an ordinary ferromagnet. The calculated total magnetic moment for $\text{Sr}_2\text{GeMoO}_6$ and $\text{Sr}_2\text{SiMoO}_6$ per formula unit is 2.00 and 1.94 μ_{B} , respectively. An integer value of the magnetic moment is a characteristic feature of HMFs. The main magnetic moment contribution comes from Mo atom, whereas the moments of the other atoms are small (Table 1).

To understand the mechanism of ferromagnetism in $\text{Sr}_2\text{GeMoO}_6$ and $\text{Sr}_2\text{SiMoO}_6$, we have to gain deep insight into the crystal-field-splitting and spin-splitting. In the following we concentrate the discussion on the properties of $\text{Sr}_2\text{GeMoO}_6$. From Fig. 1(a), the total and atom-projected DOSs of $\text{Sr}_2\text{GeMoO}_6$, we can see that, for both

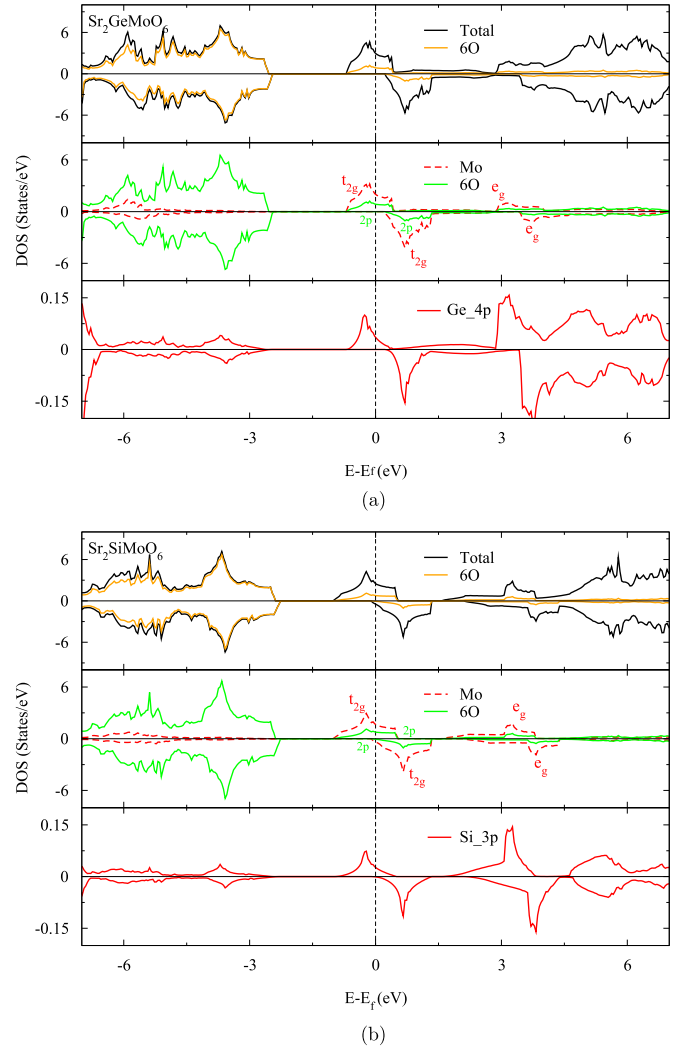


Fig. 1. Total and atom-projected DOSs of (a) $\text{Sr}_2\text{GeMoO}_6$ and (b) $\text{Sr}_2\text{SiMoO}_6$ in LSDA. The vertical dashed line denotes the Fermi energy E_f , which is set to zero.

spin-up and spin-down channels, the total DOSs of the compound are mainly composed of Mo-4d state and O-2p state around Fermi level, so we pay more attention on those states. Considering the peaks near the Fermi level, we find that the presence of an octahedral crystal field of the six oxygen atoms around Mo site results in a splitting of the five-fold degenerate Mo-4d states into doubly degenerate e_g (d_{z^2} and $d_{x^2-y^2}$) states with higher energy and triply degenerate t_{2g} (d_{xy} , d_{yz} and d_{zx}) states with lower energy for both spin-up and spin-down channels. The spin-splitting of about 0.93 eV makes the spin-up states of the triply degenerate t_{2g} cross the Fermi level, resulting in the partial occupation, and spin-down t_{2g} states are not occupied and lie at about 0.7 eV above the Fermi level. The e_g states of spin-up and spin-down lying respectively at about 3.0 and 3.5 eV are both not occupied. So the main contribution to the magnetic moment, 1.77 μ_{B} , comes from the Mo- t_{2g} states. The considerable contribution (0.14 μ_{B}) of the six O atom to the total moment results from the hybridization between the O-p and the Mo- t_{2g} states around Fermi level (Fig. 1(a)). From the DOS, we also can see that there is a weak hybridization between Ge-4p and Mo- t_{2g} states, which can influence the spin-splitting of the compound. Fig. 1(b) is total and partial DOSs of $\text{Sr}_2\text{SiMoO}_6$. The corresponding properties of $\text{Sr}_2\text{SiMoO}_6$ are similar to the properties of $\text{Sr}_2\text{GeMoO}_6$. But the both spin-up and spin-down states of the triply degenerate t_{2g} cross the Fermi level.

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