



## Research articles

Structural, electronic and magnetic properties and pressure-induced half metallicity in double perovskite  $\text{Ca}_2\text{AOsO}_6$  ( $A = \text{Cr}, \text{Mo}$ )

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## ABSTRACT

$\text{Ca}_2\text{CrOsO}_6$  was synthesized recently and measured to be an insulating ferrimagnet with a high magnetic ordering temperature of 490 K. To design a half metal, we substituted Cr with Mo and performed an investigation on  $\text{Ca}_2\text{AOsO}_6$  ( $A = \text{Cr}, \text{Mo}$ ) by using the density functional theory. However,  $\text{Ca}_2\text{MoOsO}_6$  is an insulator with a small band gap in one spin direction. By applying external pressure, the small gap can be closed, making  $\text{Ca}_2\text{MoOsO}_6$  a compensated half metal. The estimated  $T_c$  for  $\text{Ca}_2\text{MoOsO}_6$  under pressure is higher than the room temperature. Therefore, we expect that  $\text{Ca}_2\text{MoOsO}_6$  would be promising compound for spintronic devices.

## 1. Introduction

Half metallic (HM) materials, being metallic in one spin direction meanwhile insulating (or semiconducting) in the other, are expected to offer potential technological applications in the new type of spintronic devices which can generate spin-polarized currents without any external operation [1]. Besides, the HM materials possessing high magnetic ordering temperature ( $T_c$ ) have a greater advantage, since they would even open up the possibility for designing novel spintronic devices working at room temperature. Double perovskite oxide  $\text{AA}'\text{BB}'\text{O}_6$  ( $A$  and  $A'$  = alkali, alkaline-earth or rare-earth ions;  $B$  and  $B'$  = transition metals), has stable and simple crystal structure, variety choices in  $A$  and  $B$  sites, as well as stronger magnetic interactions between  $B$  and  $B'$  cations. These characters equip double perovskite to exhibit rich electronic and magnetic properties and to be an ideal system for searching high  $T_c$  HM magnets [2–14]. Among them,  $\text{Sr}_2\text{FeMoO}_6$  is the most famous for displaying an intrinsic tunneling-type magnetoresistance at room temperature, which is half metallic and has a high Curie temperature of about 410 K [15]. So far, the top two in the class of double perovskites which have the highest  $T_c$  are  $\text{Sr}_2\text{CrReO}_6$  and  $\text{Sr}_2\text{CrOsO}_6$ , having  $T_c \sim 620$  K and 725 K [4–6], respectively. However, both of them are measured to show an insulating (or semiconducting) behavior experimentally [6,16,17]. Later by chemical means of doping or substituting, researchers have realized an insulator-half metal transition based on the two, and the new designed compounds still possess a  $T_c$  well above the room temperature [8–10]. Therefore, the double perovskite oxides with high  $T_c$  are worth paying attention to, because based on them it is quite likely to obtain high  $T_c$  HM magnets by

applying suitable physical or chemical methods.

$\text{Ca}_2\text{CrOsO}_6$ , another family member in  $\text{A}_2\text{CrOsO}_6$ , was investigated by Li *et al* through first-principles calculations [18]. They assumed that  $\text{Ca}_2\text{CrOsO}_6$  has the same rhombohedral  $R\bar{3}$  structure [6,17] as  $\text{Sr}_2\text{CrOsO}_6$ . The calculated electronic structure is similar to that of  $\text{Sr}_2\text{CrOsO}_6$ . Moreover, the  $T_c$  of  $\text{Ca}_2\text{CrOsO}_6$  was estimated to be 355 K by Monte Carlo simulations. Experimentally,  $\text{Ca}_2\text{CrOsO}_6$  was synthesized recently with an order parameter of 76.2%, in order to shed light on the effect of chemical pressure on the structure and properties compared with  $\text{Sr}_2\text{CrOsO}_6$  [17]. A number of characterized techniques suggested that  $\text{Ca}_2\text{CrOsO}_6$  forms a monoclinic structure with  $P2_1/n$  symmetry instead of rhombohedral  $R\bar{3}$  structure, and is an insulating ferrimagnet with an saturation magnetic moment of  $\sim 0.2 \mu_B/\text{f.u.}$  (f.u. indicates formula unit). Importantly, the  $T_c$  of  $\text{Ca}_2\text{CrOsO}_6$  was measured to be as high as  $\sim 490$  K. This is a very attractive result, even though the compound reported in that study is not fully ordered and the influence of antisite defect on  $T_c$  does exist [19,20].

In this work, we will revisit the double perovskite  $\text{Ca}_2\text{CrOsO}_6$  to investigate its structural, electron and magnetic properties. By substituting Cr with Mo subsequently, we have designed a new compound  $\text{Ca}_2\text{MoOsO}_6$ , and explored its physical properties under ambient conditions (equilibrium volume) and under pressure, respectively, in particular the HM nature. Finally, we roughly estimated the  $T_c$  of all the compounds, expecting to obtain magnetic materials with both half metallicity and room-temperature magnetic ordering.

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## 2. Computational methods

Geometry optimizations were performed by employing Vienna Ab Initio Simulation Package (VASP) [21–24], based on the projector augmented wave (PAW) method [25,26]. For the self-consistent calculation, the plane wave cutoff energy was chosen to be 500 eV. The  $k$ -points are  $5 \times 5 \times 5$  for  $Fm\text{-}3m$ ,  $8 \times 8 \times 3$  for  $R\text{-}3$ , and  $7 \times 7 \times 5$  for  $P2_1/n$ . The convergence tolerances were selected as the difference in total energy and the maximum force being within  $1.0 \times 10^{-5}$  eV and  $1.0 \times 10^{-2}$  eV/Å, respectively.

The electronic and magnetic properties were calculated by using WIEN2K program [27,28], which is based on the full-potential linearized augmented plane wave (FP-LAPW) method. The atomic sphere radii ( $R_{\text{MT}}$ ) were 2.40, 1.95, 1.95, 2.00 and 1.60 bohrs for Ca, Cr, Mo, Os and O, respectively. In the complete Brillouin zone, 1000  $k$ -points were used. The plane wave expansion cutoff is  $R_{\text{MT}}^{\text{min}} K_{\text{max}} = 7.0$  for expanding the wave function, where  $R_{\text{MT}}^{\text{min}}$  is the atomic sphere radius,  $K_{\text{max}}$  is the plane wave cutoff. The self-consistent calculations were considered to be converged when the energy convergence was less than  $10^{-5}$  Ry/f.u. The exchange–correlation energy was treated by the generalized gradient approximation (GGA-PBE) [29]. Electron correlation for the transition elements in combination with the double-counting correlation was considered in the rotationally invariant form with a single effective Hubbard parameter  $U_{\text{eff}} = U - J$  [30], where  $U$  and  $J$  stand for Coulomb and exchange parameters, respectively. For simplicity, we used  $U$  instead of  $U_{\text{eff}}$  in the following. A series of  $U$  values are selected for transition metals, i.e., 2.0–5.0 eV for Cr and Mo, 0.5–2.0 eV for Os, while  $J = 0.0$ . These values have been adopted in related studies [31–34]. Considering the large effect of SOC on 4d and 5d atoms, it is also included to calculate the electronic and magnetic properties based on the second-variational method by using the scalar relativistic wave functions [35].

## 3. Result and discussion

### 3.1. $\text{Ca}_2\text{CrOsO}_6$

Considering the monoclinic  $P2_1/n$  structure for  $\text{Ca}_2\text{CrOsO}_6$  got in experiment [17] and rhombohedral  $R\text{-}3$  structure (cubic  $Fm\text{-}3m$  at high temperature) for  $\text{Sr}_2\text{CrOsO}_6$  [6], we have optimized all the three structures by GGA+ $U$  method. The results indicate that the  $P2_1/n$  structure is the most stable with energy difference over 150 meV/f.u. compared with the other two. It is understandable that  $\text{Ca}_2\text{CrOsO}_6$  leaves the  $R\text{-}3$  or  $Fm\text{-}3m$  symmetry due to the smaller size of  $\text{Ca}^{2+}$  cation. Similarly,  $\text{Ca}_2\text{CrWO}_6$  and  $\text{Ca}_2\text{CrReO}_6$  have also been reported to have the  $P2_1/n$  structure [2,36]. In addition, note that  $U_{\text{Cr}} = 3.0$  eV,  $U_{\text{Os}} = 1.0$  eV were chosen for the geometry optimizations and subsequent property calculations, the reasons are as follows. Firstly, the Cr–O bond length is longer than the Os–O bond length in experiment [17]. It is reasonable through comparing the radii of  $\text{Cr}^{3+}$  (0.615 Å) and  $\text{Os}^{5+}$  (0.575 Å). When using the  $U_{\text{Cr}}$  value smaller than 3.0 eV, however, the optimized Cr–O bond length is always shorter than the Os–O bond length, which is discrepant with the above analysis. Next, although the optimized crystal structures by using the  $U_{\text{Cr}}$  values larger than (or equal to) 3.0 eV give consistent electronic and magnetic properties, the larger  $U$  values we select, the more strongly lattice constants are overestimated. Thirdly, our calculations indicate that different  $U_{\text{Os}}$  has little effects on the structure and properties. In a word, the  $U$  values cannot be determined from the first-principles calculations, and usually experimental data are used to calibrate the values. Incidentally, for the following calculations on  $\text{Ca}_2\text{MoOsO}_6$  we adopted  $U_{\text{Mo}} = 3.0$  eV,  $U_{\text{Os}} = 1.0$  eV. The optimized lattice parameters for  $\text{Ca}_2\text{CrOsO}_6$  are listed in Table 1, and the experimental data taken from Ref. [17] are also listed here for comparison. It is acceptable that our lattice constants are a bit larger than the experimental ones (by 1.0% for  $a$ , 1.6% for  $b$ , 1.3% for  $c$ ) induced by the calculation methods. Here

**Table 1**

Lattice parameters for  $\text{Ca}_2\text{AOsO}_6$  ( $A = \text{Cr}, \text{Mo}$ ) optimized by GGA+ $U$  ( $U_{\text{A}} = 3.0$  eV,  $U_{\text{Os}} = 1.0$  eV). The experimental data for  $\text{Ca}_2\text{CrOsO}_6$  are taken from Ref. 17.

	$\text{Ca}_2\text{CrOsO}_6$		$\text{Ca}_2\text{MoOsO}_6$	
	Exp.	Cal.	$V_0$	$0.90 V_0$
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
$a$ (Å)	5.351	5.409	5.478	5.227
$b$ (Å)	5.456	5.546	5.676	5.554
$c$ (Å)	7.620	7.720	7.858	7.575
$V$ (Å <sup>3</sup> )	222.50	231.61	244.35	219.92
$\beta$ (°)	90.092	90.091	89.959	89.852
$A\text{-}O_1$ ( $\times 2$ , Å)	1.973	2.017	2.106	2.031
$A\text{-}O_2$ ( $\times 2$ , Å)	1.973	2.011	2.099	2.019
$A\text{-}O_3$ ( $\times 2$ , Å)	1.967	2.002	2.095	2.017
$\text{Os}\text{-}O_1$ ( $\times 2$ , Å)	1.955	1.988	1.997	1.957
$\text{Os}\text{-}O_2$ ( $\times 2$ , Å)	1.960	1.989	2.000	1.971
$\text{Os}\text{-}O_3$ ( $\times 2$ , Å)	1.946	1.984	1.996	1.961
$\angle A\text{-}O_1\text{-}O_8$ (°)	153.3	151.1	148.1	145.5
$\angle A\text{-}O_2\text{-}O_8$ (°)	152.6	150.7	147.2	145.7
$\angle A\text{-}O_3\text{-}O_8$ (°)	153.8	151.1	148.8	144.8

we have employed both the optimized and the experimental structures to calculate electronic and magnetic properties, and the results from the two are physical consistent. For simplicity, only the results from the former are given in this paper.

Study on magnetic properties in  $\text{Ca}_2\text{CrOsO}_6$  shows that the ferrimagnetic state is much more stable than ferromagnetic state (by more than 300 meV/f.u.), which is in agreement with the experimental observation [17]. Therefore, we will focus our study on ferrimagnetic phase in the following.

Fig. 1(a) presents the calculated total and partial density of states (DOS) for  $\text{Ca}_2\text{CrOsO}_6$ . We can see that the DOS of  $\text{Ca}_2\text{CrOsO}_6$  extremely resembles that of  $\text{Sr}_2\text{CrOsO}_6$  [9,37] in spite of different crystal structure. The insulating character also originates from the half filled  $\text{Cr}^{3+} t_{2g}^3$  and  $\text{Os}^{5+} t_{2g}^3$  orbitals. In fact for monoclinic  $\text{Ca}_2\text{CrOsO}_6$ , the triplet  $t_{2g}$  states of Cr (Os) split into the singlet  $d_{xy}$  and doubly degenerate  $d_{xz}/d_{yz}$  levels due to the distortion of  $\text{CrO}_6$  ( $\text{OsO}_6$ ) octahedra, whereas these bands overlap each other here, as shown the orbital-decomposed DOS in Fig. 1(b). The spin magnet moments of Cr and Os are 2.52 and 1.55  $\mu_B$ , respectively (Table 2), nearly the same as in  $\text{Sr}_2\text{CrOsO}_6$  (2.44  $\mu_B$  for Cr, 1.54  $\mu_B$  for Os, Ref. [9]). The SOC effect produces a slight large orbital moment of 0.13  $\mu_B$  on Os. Ultimately, the net magnetic moment is 0.19  $\mu_B$ , very close to the experimental value of 0.20  $\mu_B$  [17].

### 3.2. $\text{Ca}_2\text{MoOsO}_6$

For  $\text{Sr}_2\text{CrOsO}_6$ , by doping Na or La at Sr site, a half metal has been achieved successfully [8,9]. Besides that, a new compound  $\text{Sr}_2\text{MoOsO}_6$  was designed by substituting Cr with Mo [10]. In this Mo-based compound, the Mo  $t_{2g}$  orbital crosses the Fermi level and is partially occupied in contrast to the completely filling of Cr  $t_{2g}$  orbital in  $\text{Sr}_2\text{CrOsO}_6$ , owing to 4d Mo having a wider band and smaller electron correlation effect with respect to 3d Cr. The Os  $t_{2g}$  orbital in this spin direction, meanwhile, also crosses the Fermi level partially to satisfy the valence state requirement. As a result,  $\text{Sr}_2\text{MoOsO}_6$  demonstrates a HM nature, what's more, it is a compensated half metal (CHM) [31,38], i.e. half metal with zero net magnetic moment.

On the basis of the similarities between  $\text{Ca}_2\text{CrOsO}_6$  and  $\text{Sr}_2\text{CrOsO}_6$  on electron and magnetic properties, we will carry out related investigations on  $\text{Ca}_2\text{MoOsO}_6$  in order to obtain a HM magnet. Our total energy calculations show that the ground state phase for  $\text{Ca}_2\text{MoOsO}_6$  is still the  $P2_1/n$  structure. The optimized lattice parameters are listed in Table 1. The lattice constants of  $\text{Ca}_2\text{MoOsO}_6$  get increased compared with  $\text{Ca}_2\text{CrOsO}_6$ . This is natural since the radius of Mo ion (0.69 Å for

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