Effect of On-Site Coulomb Interaction on the Electronic and Magnetic Properties of Double-Perovskites \( \text{La}_2\text{CoXO}_6 \) (\( X = \text{Hf}, \text{Pt}, \text{Cd} \))

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Abstract

Electronic and magnetic properties of new double-perovskite materials \( \text{La}_2\text{CoXO}_6 \) (\( X = \text{Hf}, \text{Pt}, \text{Cd} \)) are calculated using density functional theory (DFT) and generalized gradient approximation (GGA), as well as considering onsite Coulomb interaction (GGA+U). Here, we calculated and explored the properties of \( \text{La}_2\text{CoXO}_6 \) \( (X = \text{Hafnium: Hf, Platinum: Pt, Cadmium: Cd}) \) under four possible magnetic orderings: ferromagnetic, ferrimagnetic, antiferromagnetic, and nonmagnetic. Under the GGA scheme, \( \text{La}_2\text{CoCdO}_6 \) and \( \text{La}_2\text{CoPtO}_6 \) are degenerated in the ferromagnetic and antiferromagnetic state due to the tiny energy difference. It is concluded, however, that the most stable state for \( \text{La}_2\text{CoXO}_6 \) \( (X = \text{Hf, Pt, Cd}) \) are antiferromagnetic insulators under the GGA+U scheme.

Keywords: Antiferromagnetic; Double Perovskite; On-Site Coulomb Interaction; Half Metal

Introduction

Recent advances in the field of spintronic \([1-3]\) devices, such as spin filtering tunnel junctions \([4-6]\) and magnetodielectric capacitors \([7-8]\), have sparked an interest in finding materials with stable electronic and magnetic properties. When searching for materials, double perovskites provide a crystal structure that is relatively simple and convenient for integration \([9]\). Through calculation of the electronic and structural properties of these materials, we can categorize them into several magnetic states, of which the most common are antiferromagnetic and ferromagnetic. We focus mainly on materials that show properties of an insulator, a semiconductor, or a half-metal (HM) \([10-11]\). Several ferromagnetic semiconductor materials with double perovskite structure have been previously discussed, including \( \text{La}_2\text{NiMnO}_6 \) \([12-13]\). In comparison with the ferromagnetic semiconductors or insulators, we will focus on another magnetic state: antiferromagnetic. When structuring double-perovskite materials \( A_{2}BB'O_6 \) \([14]\), \( A \) is usually exchanged with alkaline metals or rare earth metals (Ca, La, Ce etc.), and \( BB' \) is any combination of the 19 transitional metal elements from 4d and 5d. Calculating all 171 (\( C_{39}^{171} \)) combinations is very time consuming, so when searching for magnetic properties, we first used VASP code to calculate the self-consistent electronic structures. In this paper, \( A = \text{La}, \) and \( B \) is Co. Of these compounds, we have first discovered that \( \text{La}_2\text{CoZrO}_6 \) is an antiferromagnetic insulator \([15]\). For the remaining \( 17 \text{La}_2\text{CoBO}_6 \) compounds other than \( \text{La}_2\text{CoZrO}_6 \), we calculated and presented the filtered results in this paper by excluding metallic materials. To begin, we use the density functional theory to calculate and find potential insulator materials from \( \text{La}_2\text{CoXO}_6 \) \( (X = \text{Hf, Pt, Cd}) \). Due to the reason that strong electron correlation cannot be observed with GGA calculations in transition metal oxides, we have also adopted the scheme, on-site Coulomb interaction U, GGA+U \([16-17]\). The effective parameter \( U_{\text{eff}} = U – J \) is used \([18]\) in GGA+U, with \( U \) and \( J \) being coulombs and exchange parameters, respectively. In this paper, for simplicity, we use \( U \) to represent \( U_{\text{eff}} \). During the full structural optimizations, we take into account the possibilities of four distinct magnetic orderings: nonmagnetic (NM), ferromagnetic (FM), antiferromagnetic (AFM), and ferrimagnetic (FiM) phases. In the following discussion, we focus on the physical properties and correction effect on the electronic structures of three possible AFM insulators \( \text{La}_2\text{CoXO}_6 \) \( (X = \text{Hf, Pt, Cd}) \).

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Computational Method

We start with first principle DFT calculations for theoretical calculations, and we present electronic structure calculations with generalized gradient correction (GGA) [19] plus on-site Coulomb interaction U (GGA+U) [20-23]. Structural optimization calculations (i.e., relaxation for both lattice constants and atomic positions) were carried out with the all full-potential projector-augmented wave (PAW) method [24], carried out with the VASP package [25-27]. The conjugate-gradient (CG) method was used to find the stable ionic positions, and the energy convergence criteria for self-consistent calculations were set to 10^(-6) eV. We also used the 8x8x6 k-point grids in the Brillouin zone and set the cut-off energy of the plane wave basis to 450 eV. To determine the theoretical lattice constants and atomic positions through structural optimization calculations, a conjugated-gradient method was used under the conditions of forces and stresses lower than 0.03 eV/A and 0.9 kbar, respectively. We used a larger unit cell with 2 formula units (f.u.), as shown in Fig. 1a, to reduce symmetry by relaxing the structure. Table 1 lists the crystal parameters for compound La$_2$CoXO$_6$ (X = Hf, Pt, Cd) grows larger, the lattice constant and the cell volume grow larger as well.

In the first stage of our search, we used GGA method to calculate the electronic structure of La$_2$CoXO$_6$ (X = Hf, Pt, Cd), which is considered a perfectly ordered double perovskite structure (123 P4/mmm) in a NaCl configuration with the stacking of BO$_6$ and B'O$_6$ octahedral layers along the [1-11] direction. Four types of magnetic orderings (NM, FM, FiM, and AFM, as presented in Fig. 1b were examined with structural optimization calculations to find their minimum energy values. The NM state indicates that there is no spin polarization. The FM and FiM states indicate that the spin arrangements are parallel, with (B, B, B', B') = (m, m, m', m') being FM and (B, B, B', B') = (m, m, -m', -m') being FiM. The AFM state means that B and B' ion along one chain is ferromagnetic polarized, but coupling among neighbor chains is antiferromagnetic (B, B, B', B') = (m, -m, m', -m'). The up spin and down spin of the density of states are symmetrical and have a net magnetic moment of zero.

Results and Discussion

Table 2 and Table 3 show the detailed quantities of electronic and magnetic properties in the AFM and FM schemes. With GGA, La$_2$CoXO$_6$ and La$_2$CoPtO$_6$ are half-metal (HM) in the FM state, with FM and AFM energy differences of only 4 meV and 34 meV respectively. Due to the small energy difference, La$_2$CoCdO$_6$ and La$_2$CoPtO$_6$ are considered as degenerated in the ferromagnetic and antiferromagnetic state. In the antiferromagnetic scheme, all compounds show metallic attributes with GGA calculations and insulator attributes with GGA+U calculations. The calculated total spin magnetic moments are zero in the unit cell, which indicates that the systems are either insulating or half-metallic. All of the spin up and spin down gaps are around 1 eV after GGA + U, with Pt having the largest gap of 1.23 eV.

The total DOS for La$_2$CoXO$_6$ (X = Hf, Pt, Cd) in the AFM state are presented in Fig. 2, and the DOS for partial $e_g$ and $t_{2g}$ spin orbitals are presented in Fig. 3. The DOS plots for La$_2$CoXO$_6$ (X = Pt, Cd) in the FM-HM state under GGA are presented in Fig. 4 where we focus on the compounds with half metal and FM state. We list all the calculation data in the Table 2 (AFM state) and Table 3 (FM state). Density of state (DOS) for compound La$_2$CoHfO$_6$ is shown in Fig. 2a and Fig. 3a for GGA, and Fig. 2b and Fig. 3b for GGA+U. It has no GGA band gaps, but a band gap of 1.05 eV appears after GGA+U. The AFM state's total energy is 160 meV lower than FM state's for GGA, and after +U, the total energy difference becomes 677 meV, implying that La$_2$CoHfO$_6$ is stable as an AFM insulator. The charge configuration for Co is Co$^{2+}$ (3d$^7$), while the charge configuration for Hf is Hf$^{2+}$ (5d$^{19}$).

With La$_2$CoPtO$_6$, there is no band gap with GGA (Fig. 2c, Fig. 3c), but there is a band gap of 1.23 eV after GGA+U (Fig. 2d, Fig. 3d). The AFM state's total energy is only 4 meV higher than that of the FM state using GGA, indicating a metastable state. The FM state is half-metal, with an up spin band gap of 0.88 eV and a conducting down spin (Fig. 4a, Fig. 4c). Using GGA+U, the AFM state has 895 meV lower energy than the FM state, showing that La$_2$CoPtO$_6$ is highly stable as an AFM insulator. The charge configuration for Co is Co$^{2+}$ (3d$^7$), while the charge configuration for Pt is Pt$^{3+}$ (5d$^{17}$).

La$_2$CoCdO$_6$ has no band gap with GGA (Fig. 2e, Fig. 3e), and a band gap of 0.9 eV after GGA+U (Fig. 2f, Fig. 3f). The AFM state's total energy is 34 meV higher than that of the FM state before +U, indicating that the FM state is slightly more stable in the GGA configuration, with a half-metal state of 1.10 eV up spin gap and no down spin gap (Fig. 4b, Fig. 4d). However, GGA+U configurations calculate that the AFM state is more stable, with a 707 meV lower energy than the FM state. Charge configuration for Co is Co$^{2+}$ (3d$^7$), while charge configuration for Cd is Cd$^{2+}$ (4d$^{10}$). It also means that La$_2$CoCdO$_6$ is highly stable as an AFM insulator.

Conclusions

We have carried out full research of ordered double perovskites La$_2$CoXO$_6$ (X = Hf, Pt, Cd). The full structural optimization calculations results show that antiferromagnetic La$_2$CoXO$_6$ (X = Pt, Cd) is a metal in GGA configuration schemes and an insulator in GGA+U configuration schemes. La$_2$CoPtO$_6$ and La$_2$CoCdO$_6$ are slightly more stable in the FM state using GGA, showing FM half-metal characteristics. A promising candidate for AFM insulator with double perovskite structure has been designed and we hope our interesting predictions will encourage further experimental searches for similar materials.
Figure 1a. An ideal double perovskite ordered structure, La$_2$CoXO$_6$ (X = Hf, Pt, Cd), where O1(x, y, z) = (0, 0, O1z), O2(x, y, z) = (0.5, 0.5, O2z), O3(x, y, z) = (O3x, O3y, 0), O4(x, y, z) = (O4x, O4y, 0.5).

Figure 1b: The schematic diagram of 4 magnetic states: FM, FiM, AF and NM.

Figure 2. Total DOS of La$_2$CoHfO$_6$ GGA (a), GGA+U (b); La$_2$CoPtO$_6$ GGA (c), GGA+U (d); La$_2$CoCdO$_6$ GGA (e), GGA+U (f).

Figure 3. Partial DOS for $e_g$ and $t_{2g}$ spin orbitals of La$_2$CoHfO$_6$ GGA (a), GGA+U (b); La$_2$CoPtO$_6$ GGA (c), GGA+U (d); La$_2$CoCdO$_6$ GGA (e), GGA+U (f).

Figure 4. Total DOS of La$_2$CoPtO$_6$ (FM) GGA (a), La$_2$CoCdO$_6$ (FM) GGA (b); and Partial DOS for $e_g$ and $t_{2g}$ spin orbitals of La$_2$CoPtO$_6$ (FM) GGA (c), La$_2$CoCdO$_6$ (FM) GGA (d).
Table 1. Structural parameters of the possible AFM-Is and FM-HM materials in the fully optimized structure. \( \text{La}_2\text{CoXO}_6 \) are in space group (123 P4/mmm) where \( \text{La}(x, y, z) = (0, 0.5, 0.75), \text{Co}_1(x, y, z) = (0, 0, 0), \text{Co}_2(x, y, z) = (0.5, 0.5, 0.5), \text{X}_1(x, y, z) = (0.5, 0.5, 0), \text{and X}_2(x, y, z) = (0, 0, 0.5). \) \( \text{O1}(x, y, z) = (0, 0, 0), \text{O2}(x, y, z) = (0.5, 0.5, 0), \text{O3}(x, y, z) = (0.3x, 0.3y, 0). \) \( \text{O4}(x, y, z) = (0.4x, 0.4y, 0.5). \)

<table>
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<tr>
<th>\text{La}_2\text{CoXO}_6</th>
<th>\text{Hf}</th>
<th>\text{Pt}</th>
<th>\text{Cd}</th>
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<tr>
<td>a (Å)</td>
<td>5.691</td>
<td>5.600</td>
<td>5.645</td>
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<tr>
<td>c/a</td>
<td>1.414</td>
<td>1.421</td>
<td>1.415</td>
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<td>( V_0/f .u. )</td>
<td>130.317</td>
<td>124.753</td>
<td>127.210</td>
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Table 2. Calculated physical properties of the \( \text{La}_2\text{CoXO}_6 \) (X = Hf, Pt, Cd) with double perovskite structure in the full structural optimization calculation of GGA (0, 0) and GGA+U (5, 2), by the AFM scheme.

<table>
<thead>
<tr>
<th>Materials ( \text{La}_2\text{CoXO}_6 )</th>
<th>(Co, X)</th>
<th>Spin magnetic moment (μB/f.u.)</th>
<th>( d ) orbital electrons ↑/↓</th>
<th>Band Gap (eV)</th>
<th>ΔE (meV/f.u.)</th>
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<tr>
<td>( \text{Hf} )</td>
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<td>0.934</td>
<td>0.013</td>
<td>0</td>
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<td></td>
<td>(5, 2)</td>
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<td>0.028</td>
<td>0</td>
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<td>( \text{Pt} )</td>
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<td>0</td>
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<td>(5, 2)</td>
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<td>0.06</td>
<td>0</td>
<td>4.925/2.330</td>
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<td>( \text{Cd} )</td>
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<td>0</td>
<td>4.018/3.200</td>
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<td>(5, 2)</td>
<td>1.044</td>
<td>-0.003</td>
<td>0</td>
<td>4.136/3.103</td>
</tr>
</tbody>
</table>

Table 3. Calculated physical properties of \( \text{La}_2\text{CoXO}_6 \) (X = Hf, Pt, Cd) in double perovskite structure, with the full structural optimization of GGA (0, 0) and GGA+U (5, 2) in the FM scheme.

<table>
<thead>
<tr>
<th>Materials ( \text{La}_2\text{CoXO}_6 )</th>
<th>(Co, X)</th>
<th>Spin magnetic moment (μB/f.u.)</th>
<th>( d ) orbital electrons ↑/↓</th>
<th>Band Gap (eV)</th>
<th>ΔE (meV/f.u.)</th>
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<td>( \text{Hf} )</td>
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<td>3.000</td>
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<td>(5, 2)</td>
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<td>4.970/2.254</td>
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<td>( \text{Pt} )</td>
<td>(0, 0)</td>
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<td>0.251</td>
<td>3.000</td>
<td>4.764/2.461</td>
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<td>0.237</td>
<td>3.000</td>
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<td>1.000</td>
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Acknowledgements

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