Antiferromagnetic Insulator Double Perovskite 
\( \text{La}_2\text{CoZrO}_6 \)

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**Introduction**

Recently, magnetic half-metals have been in high interest in spintronic applications [1], such as magneto dielectric capacitors [2-3] and spin filtering tunnel junctions [4-8]. Double perovskites, compared with other complex crystal structures, are relatively simple and convenient for integration [9]. Double perovskite half-metals have three attributes:

1. Quantization of the magnetic moment
2. 100% spin polarization at the Fermi level
3. Zero spin susceptibility

Their special attributes have brought about many experimental and theoretical researches, with various findings including Ferromagnetic half-metals with near room temperature Curie temperatures found in ordered double perovskites such as \( \text{La}_2\text{NiMnO}_6 \) (TC=280K) [10] and \( \text{Bi}_2\text{NiMnO}_6 \) (TC=340K) [11]. However, some double perovskite magnetic insulators are antiferromagnetic (AFM) and not ferromagnetic (FM), such as in the cases of \( \text{La}_2\text{YTaO}_6 \) and \( \text{La}_2\text{VCuO}_6 \) [12]. In many cases, the existence of half-metal (HM) is related to double-exchange or super exchange interactions. \( \text{Sr}_2\text{CoZrO}_6 \) and \( \text{A}_2\text{CrRuO}_6 \) (A=Si, Ge, Sn, and Pb) are both half-metals attributed to super exchange and generalized double-exchange mechanism [4,13]. When structuring \( \text{A}_2\text{BF}_6 \)-half-metal materials [14], A is usually exchanged with alkaline metals or rare earth metals (Ca, La, Ce etc.), while A=La in this paper. BB’ can be any combination of the 29 transitional metal elements other than A (Ca, Ce etc.). It is a time-consuming task to calculate the 406 \( \binom{29}{2} \) combinations, and when searching for magnetic properties, we first used VASP code to calculate the self-consistent electronic structure of all 406 \( \text{La}_2\text{BB’O}_6 \) compounds. Fuh et al. [15] have mentioned that the states of FM-semiconductor states in the BB’ pairs of Fe (Co, Rh, Ir) are stable against antiferromagnetism and hence we do not consider them any further.

The aim of this paper is to search for new antiferromagnetic insulators from double-perovskite oxides. Here, we use first principle theory to calculate and explore potential insulating material \( \text{La}_2\text{CoZrO}_6 \). In transition metal oxides, the fact that strong electron correlation cannot be observed with GGA calculations should be corrected with GGA+U [16-19]. In GGA+U, the effective parameter \( U_{\text{eff}}=U-J \) is used [16], with U and J being coulombs and exchange parameters, respectively. In this paper, for simplicity, we use U to represent \( U_{\text{eff}} \). In the following discussion, we focus on the physical properties and correction effect on the electronic structures of possible AFM insulator \( \text{La}_2\text{CoZrO}_6 \).

**Discussion**

**Computational method**

The first principle DFT calculations for theoretical calculations and the electronic structure calculations with generalized gradient correction (GGA) [17] plus on-site Coulomb interaction U (GGA+U) [18-20] are used. 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) [21,22] method, carried out with the VASP package [23,24]. We used the conjugate-gradient (CG) method 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 $8\times8\times6$ 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/Å and 0.9 kBar, respectively. To reduce symmetry by relaxing the structure, we used a larger unit cell with two f.u., as shown in Figure 1. The crystal parameters from full optimization calculations are listed in Table 1. La$_2$CoZrO$_6$ has a c/a ratio close to the ideal value of $\sqrt{2}$, meaning that the structural shape is close to the ideal double perovskite structure. We not only carried out full structural optimizations, but also put into consideration the possibility of four distinct magnetic orderings: nonmagnetic (NM), ferromagnetic (FM), ferrimagnetic (FiM), and antiferromagnetic (AFM) phases in Figure 2.

![Figure 1: An ideal double perovskite ordered structure, La$_2$CoZrO$_6$, where there are 4 kinds of O, O1(0, 0, 0.2434), O2(0.5, 0.5, 0.2566), O3(0.2428, 0.2428, 0), O4(0.2572, 0.2572, 0.5).](image)

Table 1: Structural parameters of the possible AFM-Is material in the fully optimized structure.

| La2CoZrO6 | a (Å) | 5.6623 |
| c/a | 1.4173 |
| V0/f.u. | 126.8854 |
| O1 | (0, 0, 0.2434) |

La$_2$CoZrO$_6$ are in space group (123 P4/mmm) where La(x, y, z) = (0, 0.5, 0.75), Co$_1$(x, y, z) = (0, 0, 0), Co$_2$(x, y, z) = (0.5, 0.5, 0), Zr$_1$(x, y, z) = (0.5, 0.5, 0), and Zr$_2$(x, y, z) = (0, 0, 0.5). O1(x, y, z) = (0, 0, 0.12). O2(x, y, z) = (0.5, 0.5, 0). O3(x, y, z) = (0.3x, 0.3y, 0). O4(x, y, z) = (0.4x, 0.4y, 0.5).

Results

Table 2: Calculated physical properties of the La$_2$CoZrO$_6$ in double perovskite structure in the full structural optimization calculation of GGA (+U).

| Material | U(Co, Zr) | Spin Magnetic Moment (μB/ f.u.) | d Orbital Electrons | Band Gap | ∆E (meV/ f.u.) |
|----------|-----------|-------------------------------|--------------------|----------|---------------|
| La$_2$CoZrO$_6$ | (0, 0) | mCo: 0.93, mZr: 0.012, mtot: 0 | Co: 4.136/3.211, Zr: 0.845/0.835 | 0.00/0.00 | -219 |
| La$_2$CoZrO$_6$ | (5, 2) | mCo: 2.696, mZr: 0.026, mtot: 0 | Co: 4.987/3.211, Zr: 0.807/0.791 | 0.95/0.95 | -647 |

AFM: Antiferromagnetic; FM: Ferromagnetic

Table 2 shows the calculated quantities of electronic and magnetic properties. In the AFM ordering, La$_2$CoZrO$_6$ shows conducting metal and insulating attributes in the GGA and GGA+U scheme respectively. La$_2$CoZrO$_6$ has the lowest energy state in the AFM-Is ordering under GGA+U, at 647 meV below the FM state's energy. With GGA, in the AFM ordering, La$_2$CoZrO$_6$ is conducting in both spin channels, resulting in a metal, at 219 meV below the FM state’s energy. The band gap for both spin channel opens to 0.95 eV in the AFM ordering after +U, resulting in an AFM insulator.
The total DOS in the GGA scheme for La$_2$CoZrO$_6$ is presented in Figure 3a, and the total DOS in the GGA+U scheme for La$_2$CoZrO$_6$ is presented in Figure 3b. The charge configuration in GGA is Co$^{2+}$ (3d$^{4.03}$) and Zr$^{2+}$ (4d$^{1.68}$). The charge configuration in GGA+U is Co$^{1.702}$ (3d$^{4.298}$) and Zr$^{2.402}$ (4d$^{1.599}$).

**Figure 3a:** Total DOS of AFM-state La$_2$CoZrO$_6$ in the GGA scheme.

**Figure 3b:** Total DOS of AFM-state La$_2$CoZrO$_6$ in the GGA+U scheme.

**Conclusion**

We have carried out full research of ordered double perovskite La$_2$CoZrO$_6$. The full structural optimization calculations results show La$_2$CoZrO$_6$ has potential to be an antiferromagnetic insulator. According to the energy levels, AFM-1s is the most stable state. We hope that these findings can encourage further experimental research on antiferromagnetic insulators.

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