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Short Communication

Antiferromagnetic Insulator Double Perovskite La_2CoZrO_6

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Abstract

Density functional theory and generalized gradient approximation (GGA) with onsite Coulomb interaction (GGA+U) is used to calculate the magnetic properties of new material La_2CoZrO_6. Here, we considered the possibilities of four magnetic orderings: ferromagnetic, ferrimagnetic, antiferromagnetic, and nonmagnetic states. Under the GGA+U scheme, we finally find that the antiferromagnetic insulator stands out as the most stable state among these four states.

Keywords: Half-metal; Double perovskite; First principle calculations

Abbreviations: AFM: Antiferromagnetic; HM: Half Metal; IS: Insulator; FM: Ferromagnetic

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 La_2NiMnO_6 (TC=280K) [10] and Bi_2NiMnO_6 (TC=340K) [11]. However, some double perovskite magnetic insulators are antiferromagnetic (AFM) and not ferromagnetic (FM), such as in the cases of La_2VTcO_6 and La_2VCuO_6 [12]. In many cases, the existence of half-metal (HM) is related to double-exchange or super exchange interactions. Sr_2CoZrO_6 and A_2CrRuO_6 (A=Si, Ge, Sn, and Pb) are both half-metals attributed to super exchange and generalized double-exchange mechanism [4,13]. When structuring $A_2BB'O_6$ 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 C_2^{29} combinations, and when searching for magnetic properties, we first used VASP code to calculate the self-consistent electronic structure of all 406 $La_2BB'O_6$ 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 La_2CoZrO_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_{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_{eff}. In the following discussion, we focus on the physical properties and correction effect on the electronic structures of possible AFM insulator La_2CoZrO_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*8*6 k-point grids in the Brillouin zone and set the cut-off energy of the plane wave basis to 450eV. 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 0.03eV/A and 0.9kBar, 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_2CoZrO_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.

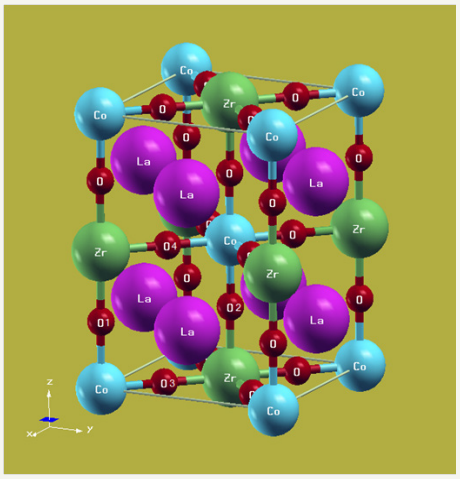

Figure 1: An ideal double perovskite ordered structure, La_2CoZrO_6, where there are 4 kinds of O, O1(0, 0, 0.2434), O2(0.5, 0.5, 0.2566), O3(0.2428, 0.2428, 0), O4(0.2572, 0.2572, 0.5).

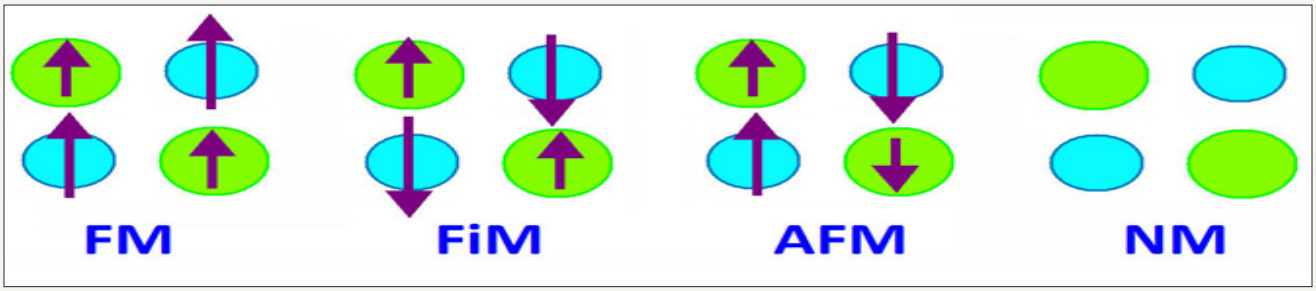

Figure 2: The schematic diagram of 4 magnetic states: FM, FiM, AF and NM.

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)
O2	(0.5, 0.5, 0.2566)
O3	(0.2428, 0.2428, 0)
O4	(0.2572, 0.2572, 0.5)

La_2CoZrO_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, 0.5), 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, 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).

Results

Table 2: Calculated physical properties of the La_2CoZrO_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	ΔE (meV/f.u.)
		mCo	mZr	mtot	Co	Zr	(eV)	AFM-FM
La_2CoZrO_6	(0, 0)	0.93	0.012	0	4.136/3.211	0.845/0.835	0.00/0.00	-219
La_2CoZrO_6	(5, 2)	2.696	0.026	0	4.987/2.311	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_2CoZrO_6 shows conducting metal and insulating attributes in the GGA and GGA+U scheme respectively. La_2CoZrO_6 has the lowest energy state in the AFM-Is ordering under GGA+U, at 647meV below the FM state's energy. With GGA, in the AFM ordering, La_2CoZrO_6 is conducting in both spin channels, resulting in a metal, at 219meV below the FM state's energy. The band gap for both spin channel opens to 0.95eV in the AFM ordering after +U, resulting in an AFM insulator.

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The total DOS in the GGA scheme for La_2CoZrO_6 is presented in Figure 3a, and the total DOS in the GGA+U scheme for La_2CoZrO_6 is presented in Figure 3b. The charge configuration in GGA is $Co^{1.653}$ ($3d^{7.347}$) and $Zr^{2.320}$+ ($4d^{1.680}$). The charge configuration in GGA+U is $Co^{1.702}$ ($3d^{7.298}$) and $Zr^{2.402}$+ ($4d^{1.598}$).

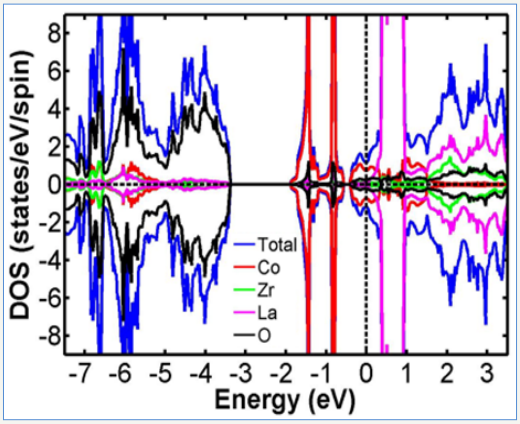

Figure 3a: Total DOS of AFM-state La_2CoZrO_6 in the GGA scheme.

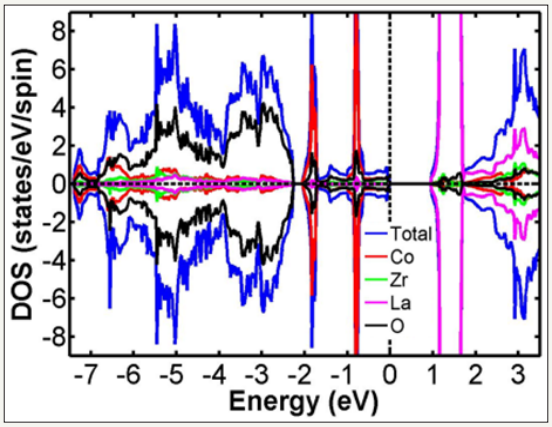

Figure 3b: Total DOS of AFM-state La_2CoZrO_6 in the GGA+U scheme.

Conclusion

We have carried out full research of ordered double perovskite La_2CoZrO_6. The full structural optimization calculations results show La_2CoZrO_6 has potential to be an antiferromagnetic insulator. According to the energy levels, AFM-Is is the most stable state. We hope that these findings can encourage further experimental research on antiferromagnetic insulators.

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