First-principles investigation of electronic and magnetic properties of double perovskite CaFeTi$_2$O$_6$

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HIGHLIGHTS

- Electronic and magnetic properties of CaFeTi$_2$O$_6$ are investigated.
- The ferromagnetic and antiferromagnetic states are competitive.
- Half metallicity is found for the oxide.
- The half metallicity is due to different orbital occupations of iron.

GRAPHICAL ABSTRACT

We investigate electronic and magnetic properties of CaFeTi$_2$O$_6$ and predict that it is a half metal. The half metallicity is attributed to different orbital occupations arising from the different coordination geometries of Fe^{2+}. The degeneracy of 3d_{xz} and 3d_{yz} orbitals within the square-planar Fe^{2+} is found to play a crucial role in realizing the half metallicity.
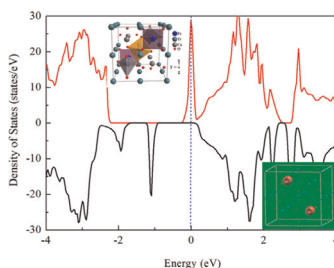
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ABSTRACT

We perform a first-principles investigation of the electronic structures and magnetic properties of a double perovskite CaFeTi$_2$O$_6$, in which one Fe^{2+} ion is in a square-planar coordination and the other is in a tetrahedral coordination. We show that the ferromagnetic and antiferromagnetic states of CaFeTi$_2$O$_6$ are energetically competitive with the Fe^{2+} in a high-spin state. The oxide is also found to show a half-metallic character, which is attributed to the different orbital occupations of the Fe^{2+} ions. In addition, the energy degeneracy of the 3d_{xz} and 3d_{yz} orbitals in the square-planar Fe^{2+} is found to play a crucial role in realizing the half metallicity.

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1. Introduction

Half-metallic materials, which are metallic in one spin channel while insulating in the other, are viewed as key ingredients for future high-performance spintronics devices due to their completely polarized spins at Fermi level without any external stimuli. Double perovskites often show various technologically important properties, e.g. half metallicity, multiferroicity, ferroelectricity, piezoelectricity, ferromagnetism and colossal magnetoresistance [1–8]. For instance, La$_2$NiMnO$_6$ and La$_2$CoMnO$_6$ have been identified to be ferromagnetic insulators with Curie temperature close to room temperature [9–11]. Bi$_2$NiMnO$_6$, on the other hand, has been proved to be a new multiferroic (ferromagnetic, ferroelectric) material [5]. Especially, since the first discovery of the colossal magnetoresistance in the Sr$_2$FeMoO$_6$ [6], which

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serves as a half-metallic ferrimagnet, much effort has been devoted to seeking half metals within the family of double perovskites. Recently, K_2MnRhO_6 and La_2CrWO_6 have also been predicted to be viable candidates as half metals [12].

Double perovskites usually have a general formula of $A_2BB'O_6$ or $AA'BB'O_6$, in which the BO_6 and $B'O_6$ octahedra are arranged in a rocksalt configuration. However, Leinenweber et al. [13,14] synthesized another unique double perovskite $CaFeTi_2O_6$ with a tetragonal structure, in which the B sites are fully occupied by nonmagnetic Ti ions and the A sites are filled by Fe ions. This atomic configuration differs markedly from the general formula of $A_2BB'O_6$ and $AA'BB'O_6$, in which the A sites are filled by nonmagnetic ions while the B sites are magnetic ions. It therefore arouses great interest to probe the relationships between structural features and magnetic properties of $CaFeTi_2O_6$. In particular, in $CaFeTi_2O_6$, one Fe^{2+} is in a square-planar geometry, while the other is in a tetrahedral geometry owing to the heavily tilted geometries of the TiO_6 octahedra. Furthermore, the d orbitals of transition metals in the oxide split into different electronic configurations under crystal fields, mediating property shift. These highlight the importance in investigating theoretically electronic and magnetic properties of $CaFeTi_2O_6$. For these reasons, we investigate electronic and magnetic properties of $CaFeTi_2O_6$ by density-functional-theory (DFT) calculations, and predict that the $CaFeTi_2O_6$ is a half metal with energetically competitive ferromagnetic and antiferromagnetic states.

2. Computational details

Calculations of energies and electronic structures were conducted with WIEN2K package [15,16], which is based on full-potential linearized augmented plane wave plus local orbitals (FP-LAPW+lo) [17,18]. The generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof scheme [19] was adopted as the exchange correlation potential. The values of the atomic sphere radii (R_{MT}) were chosen as 2.44, 1.99, 1.91, and 1.70 a.u. for Ca, Fe, Ti and O, respectively. The plane wave expansion cutoffs are 7.0 for expanding the wave function (RK_{MAX}) and 14.0 for expanding the densities and potentials (G_{MAX}). In the Brillouin zone, a total of 1000 k points were adopted. The Brillouin zone integration was carried out with the modified tetrahedron method [20]. Self-consistency was achieved when the total energy was converged to be smaller than 10^{-5} Ry/f.u. To properly address the strong electron correlation of the 3d transition metals (Fe in our case) [21], the GGA plus on-site repulsion U method (GGA+U) was applied [22–24]. The effective $U_{eff} = U - J$ was adopted, where U and J were the Coulomb and exchange parameters, respectively. For simplicity, the U was adopted to represent the effective parameter U_{eff}. Here, a series of U values have been chosen for Fe 3d orbitals to improve the credibility of our calculations.

3. Results and discussion

$CaFeTi_2O_6$ crystallizes in a unique tetragonal double perovskite structure within the $P4_2/nmc$ space group (No. 137) [25], and there are four Ca, four Fe, eight Ti atoms, and twenty four O atoms in each unit cell. Fig. 1 shows its atomic structure, where two Fe^{2+} are in tetrahedral geometries (2.097 Å for the Fe–O bond), while the others are in square-planar geometries (2.084 Å for the Fe–O bond) due to the significantly tilted geometries of the TiO_6 octahedral frameworks. Generally, in almost all of the ferrites, iron ions are exclusively coordinated in three-dimensional polyhedra, e.g. tetrahedra and octahedra. However, one Fe ion in $CaFeTi_2O_6$ is coplanar with four oxygen atoms and the square is undistorted.
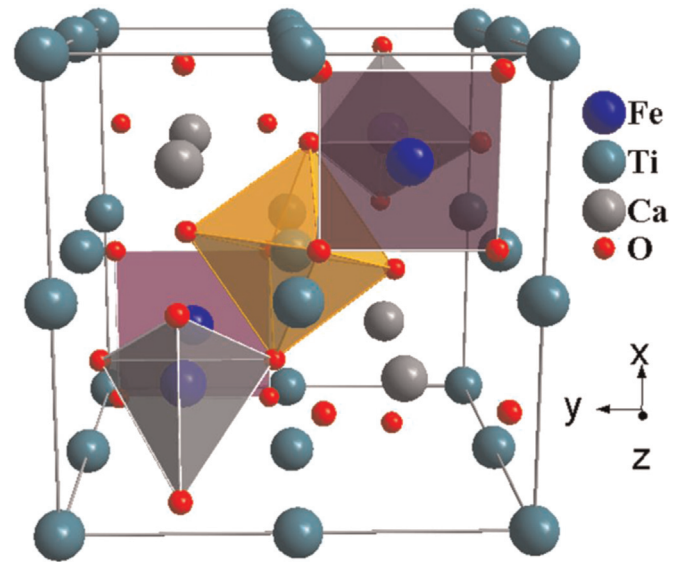
Fig. 1. Crystal structure of the $CaFeTi_2O_6$. The polyhedra in gray, purple, and orange indicate the FeO_4 tetrahedra, FeO_4 quadrilatera, and TiO_6 octahedra, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

For simplicity, we hereafter take Fe1 to stand for the Fe in the tetrahedral geometry and Fe2 to stand for the Fe in the square-planar geometry. Both the Fe and Ca ions are ordered along the c axis. The Ca ions are located at the irregular site on the 4_2 screw axis with the Ca–O distance ranging from 2.3 Å to 2.7 Å. The Fe ions, on the other hand, sit at two distinct sites within the $m2$ symmetry and alternate along the $\bar{4}$ axis.

The experimentally observed crystal structure [25] is adopted in the calculations, i.e. one $CaFeTi_2O_6$ unit cell is adopted, as shown in Fig. 1. To investigate the transport and magnetic property, we design three possible magnetic configurations: (i) ferromagnetism (FM) in which the Fe ions are arranged in a parallel way, (ii) antiferromagnetism I (AFMI) in which the Fe1 and Fe2 ions are arranged in a antiparallel way, and (iii) antiferromagnetism II (AFMII) in which magnetic moments of Fe1 and Fe2 ions are arranged in a antiparallel way and are at their respective sites. Our results reveal that the AFMII state has a much higher energy than the rest two states (70~80 meV/f.u.). The energy difference between the FM and AFMI states (Table 1) is small, ranging from 5.1 to -2.2 meV as U value changes from 0 to 5 eV (taking FM state as the energy reference). In particular, the FM state is stable than the AFMI state when the U is no more than 3 eV, while the AFMI phase is energetically more preferred than the FM phase when the U is more

Table 1
The calculated energy differences (ΔE) between the FM and AFM1 configurations (in meV per formula unit, taking the FM state as an energy reference). The total magnetic and corresponding magnetic moments for Fe and O ions are also listed. Calculations are conducted using the GGA+U with the U ranging from 0.0 to 5.0 eV for Fe.

U (eV)	M (μ_B)					ΔE (meV/f.u.)
		Fe1	Fe2	O	Total	
0	FM	3.49	3.46	0.04	16.0	5.1
	AFM1	3.48	−3.45	0.03	0.12	
3	FM	3.56	3.64	0.04	16.0	0.6
	AFM1	3.56	−3.64	0.01	0.0	
4	FM	3.58	3.69	0.03	16.0	−0.8
	AFM1	3.58	−3.69	0.01	0.0	
5	FM	3.60	3.74	0.03	16.0	−2.2
	AFM1	3.60	−3.74	0.01	0.0	