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Stability of half-metallic antiferromagnet La_2VMnO_6, first-principles calculation study

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ABSTRACT

The double perovskite La_2VMnO_6 with a $Fm\overline{3}m$ structure was predicted by Pickett et al. as a half-metal (HM) antiferromagnet (AFM) based on first principle calculations, while Androulakis et al.'s experimental result showed that La_2VMnO_6 also exhibits the same structure as a ferrimagnetic (FiM) state. For thoroughly understanding what happens in the double perovskite La_2VMnO_6 with a $Fm\overline{3}m$ structure, we first calculated the fixed cubic $Fm\overline{3}m$ structure before recalculating the structure through an optimization process. Our results show that La_2VMnO_6 is a FiM state when found in the fixed and volume-relaxed cubic $Fm\overline{3}m$ structure. However, after full relaxation, it becomes a HM-AFM and remains the same state even on-site Coulomb interactions ($+U$) are taken into consideration. This recalculation illustrates that the magnetic state of the Mn ion is sensitive to the crystal field of MnO_6 octahedron, and is the main reason behind the transformation of the magnetic state of La_2VMnO_6 from a FiM to a AFM state after full relaxation. Because the difference of total energy $\Delta E^{FiM-AFM}$ is small (merely about 57.1 meV/f.u.) and shows up as nearly the same space group in both FiM and AFM states La_2VMnO_6, we conclude that in which state it is mainly determined by the crystal field of the MnO_6 octahedron, i.e. the distortion magnitude of the MnO_6 octahedron, which is related to the process of synthesis. Although Androulakis et al.'s experimental result show that this is a $Fm\overline{3}m$/FiM state, we think that it is still possible for a I4/mmm/AFM state to exists, i.e. a HM-AFM La_2VMnO_6.

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1. Introduction

In 1983, de Groot et al. [1] discovered half-metallic (HM) ferromagnets (FM) by calculating the band structure of the magnetic semi-Heusler compounds NiMnSb and PtMnSb. There are several characteristic properties in HM materials, included 100% spin-polarization at the Fermi level, quantized spin magnetic momenta and zero spin susceptibility. Because of their single-spin charge carriers, HM materials can be applied as single-spin electron sources and high-efficiency magnetic sensors [2–4]. HM materials in which the total magnetic moment is zero are called HM antiferromagnets (AFM). Lacking a macroscopic magnetic field, HM-AFM materials can transport a 100% spin-polarized charge without any net magnetization. HM-AFMs have several applications; for example, they can be used as probes in spin-polarized scanning tunneling microscopes without perturbing the spin character of samples. Combining with these factors, they also play an important role in spintronic devices. The first HM-AFM was proposed by van Leuken and de Groot [5] in 1995.

In 1998, Pickett [6] first systematically looked for HM-AFMs by the (fixed) cubic double perovskite structure. He proposed La_2VMnO_6 as one of the promising candidates for a HM-AFM. Some other possible double perovskite structure HM-AFM candidates were predicted laterly, such as $LaAVRuO_6$ [7], $LaAVMoO_6$ [8], $LaAVOsO_6$, $LaAMoYO_6$ [9] (A=Ca, Sr, Ba and Y=Re and Tc), La_2VTcO_6 and La_2VCuO_6 [10]. In this compound with HM-AFMs, V and Mn are aligned with antiparallely magnetic moments that exactly cancel each other out. This finding is based on the assumptions that both V and Mn are trivalents, and that all Mn ions are in a low spin state of $S=1$ ($t_{2g}^3\uparrow e_g^1\downarrow$). However, Androulkis et al. [11] synthesized La_2VMnO_6 samples, which had a cubic $Fm\overline{3}m$, partially ordered double perovskite structure. The structure exhibited a ferrimagnetic (FiM) state rather than an antiferromagnetic (AFM) state, implying that its Mn and V ions are trivalent, and that Mn^{3+} is in a high spin state.

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Motivated by the theoretical and experimental works mentioned above, we have not only performed electronic structure calculations for a fixed crystal with Fm$\overline{3}$m, but also carried out full structural optimization. We find that the double perovskite La_2VMnO_6 is FiM if we use only volume relaxation without atomic position relaxation. The same result obtained in previous experiments [11]. However, after full structural optimization, we found that La_2VMnO_6 changes to a I4/mmm structure and reveal a HM-AFM property, while Mn^{3+} appears in a low spin state. We also did GGA $+U$ calculation because of rather strong correlation effect of transition metal oxides. It still remained a HM-AFM property after calculations.

2. Method

The calculations were used here, based on density functional theory (DFT) [12] with the generalized gradient approximation (GGA) [13]. Our calculations were performed by using the WIEN2k package [14] with the all electron full-potential linearized augmented plane wave (FLAPW) method [15,16] in which the FLAPW method makes no shape approximation to the electron density or potential and retains high variational freedom in all regions. The cutoff angular momentum (L_{max}) of 10 for the wave function and of 6 for the charge density and potential were sufficient for performing accurate total-energy calculations [14]. The number of augmented plane waves was about 145 per atom, i.e. $R_{mt}\cdot K_{max}=7$. The muffin-tin sphere radii were set to 2.5 a.u. for La, 2.1 a.u. for V, Mn, and 1.5 a.u. for O [17]. The improved tetrahedron method was used to perform Brillouin-zone (BZ) integration [18] and 120 and 163 k-points were used in the irreducible Brillouin-zone (IBZ) wedge for the Fm$\overline{3}$m and I4/mmm structures. In the process of structure optimization calculations, the faster frozen-core full-potential projection augmented wave (PAW) method [19] was used as implemented in the VASP package [20] in which the BZs were sampled with a 886 Monkhorst-Pack grid (30 k-points in the IBZ). A cutoff energy of 450 eV was set for plane waves. With the process of optimization, their atomic positions and lattice constants were fully relaxed by means of a conjugate gradient technique. Theoretical equilibrium structures were obtained when the forces acting on all the atoms and the stresses were less than 0.01 eV/Å and 1.2 kbar, respectively. Because that the La_2VMnO_6 are transition metal oxide, we have to consider the strong correlation effects that are set by GGA $+U$ calculation [21,22], including on-site U (Coulomb repulsion)$=$2.0 eV and J (Hund's rule exchange)$=$0.87 eV for V 3d electrons and U=3.0 eV and J=0.87 eV for Mn 3d electrons [7,23].

3. Results and discussion

3.1. Electronic structure and magnetic properties

We undertook calculations of the initial arranged FM and AFM states with volume relaxation and full structure relaxation in [1 1 1] the stacked double perovskites La_2VMnO_6 (see Fig. 1). The calculated physical properties are listed in Table 1. Volume relaxation with fixed atomic positions in the ideal perovskite structure results in a Fm$\overline{3}$m space group. However, after full structure relaxation, the ideal perovskite structure changes into the I4/mmm space group. We find that the initial arranged AFM state of the Fm$\overline{3}$m space group La_2VMnO_6 converged to the FiM state, therefore, we have labeled it as AFM/FiM magnetic state. $\Delta E^{FM(FiM)-AFM}$ is the energy difference between the FM (or FiM) state and AFM state. One can see that the FiM state with a Fm$\overline{3}$m space group structure (the same magnetic state and structure with the Androulakis et al.'s experimental result [11]) is more stable than the FM state. However, the most stable structure is the AFM state with a I4/mmm space group. As such, this is why GGA $+U$ calculations were only for this structure (data in brackets). The corresponding total and orbital-decomposed density of states (DOS) are displayed in Figs. 2–4. We will focus our discussions on the FiM and AFM states of La_2VMnO_6. According to our calculated results of the total magnetic moment (m_t) and DOS in Fermi level ($N(E_F)\uparrow,\ \downarrow$), we can see that the most stable structure of La_2VMnO_6 has a HM-AFM property. As shown in Fig. 3, there is a band gap of about 1.36 eV in the spin-up channel and no band gap on the spin-down channel near the Fermi level, showing a half-metallic property exists in La_2VMnO_6.

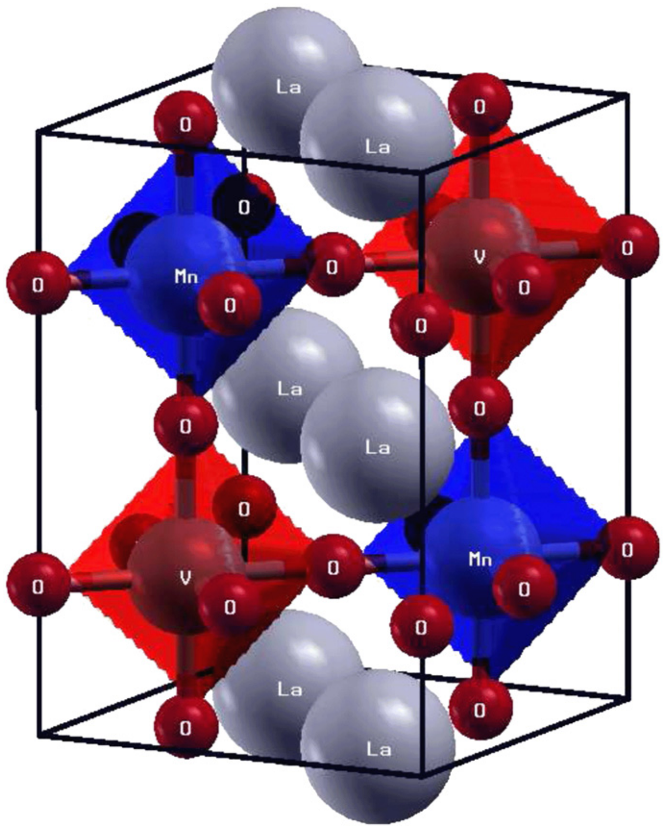

Fig. 1. The double perovskites La_2VMnO_6 with [1 1 1] stacked structure (10 atoms/unit cell).

The ionic picture of La_2VMnO_6 is $La_2^{3+}V^{3+}Mn^{3+}O_6^{2-}$ means that the transition metal atoms V and Mn have the valence configuration of $V^{3+}(3d^2)$ and $Mn^{3+}(3d^4)$. If we consider AFM coupling, the electronic structures are V^{3+} ($t_{2g}^2\downarrow, S=-1$) and Mn^{3+} ($t_{2g}^3\uparrow e_g^1\downarrow, S=1$). They exist in a low spin state with zero total magnetic moment, which is consistent with the results of Pickett et al. [6]. If we consider the high spin state, however, Mn^{3+} is in a ($t_{2g}^3\uparrow e_g^1\uparrow, S=2$) configuration, which results in a FiM state, as found in Androulakis et al.'s experiment [11]. In our calculations, in a AFM state with the I4/mmm structure, the occupation numbers at the V-site are 0.57e (spin-up) and 2.09e (spin-down), while at the Mn-site they are 3.24e (spin-up) and 1.52e (spin-down), respectively (see Table 1). Therefore, the charge configurations here are $V^{2.34+}(3d^{2.66})$ and $Mn^{2.25+}(3d^{4.75})$, respectively. Because of the hybridization between V 3d (Mn 3d) and O 2p orbitals, the ionic number of V (Mn) is not an integer. One can see that Δ_{CF} of the MO_6 octahedron in Fig. 3 is slightly larger than that in Fig. 2. Fig. 3 also shows that the Mn ion is in a low spin state when found in a I4/mmm structure

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