Magnetic coupling mechanism in *A*-site ordered perovskite YMn$_3$Al$_4$O$_{12}$: Extended (Mn−O)−(O−Mn) superexchange

Hongping Li [a,b], Xiaojuan Liu [a,*], Changsheng Li [b], Shuhui Lv [c], Yijia Bai [a], Zhongchang Wang [c,**], Jian Meng [a,*]

[a] State Key Laboratory of Rare Earth Resources Utilization, Changchun Institute of Applied Chemistry, University of Chinese Academy of Sciences, 5625 Renmin Street, Changchun, Jilin 130022, PR China
[b] School of Material Science and Engineering, Jiangsu University, Zhenjiang 212013, PR China
[c] WPI Research Center, Advanced Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

ARTICLE INFO

ABSTRACT

A-site ordered double perovskites hold promise for potential device applications, where how their magnetic objects actually interact is known to influence functionality. Here, we investigate, by first-principles calculations, electronic and magnetic properties of YMn$_3$Al$_4$O$_{12}$, and demonstrate that it is an antiferromagnetic insulator. Our calculations reveal the extended (Mn−O)−(O−Mn) superexchange as a primary magnetic coupling mechanism in YMn$_3$Al$_4$O$_{12}$, and further identify the O−O bonds as a key factor to dominate coupling strength. We suggest that this superexchange mode is the origin of anti-ferromagnetic behavior, opening an additional avenue to understand magnetic coupling in *A*-site ordered double perovskites.

1. Introduction

A-site ordered double perovskites, *A*′A$_3$B$_4$O$_{12}$, have aroused extensive attention recently owing to their unique structures and for their wide variety of intriguing physical properties [1−9]. They usually crystallize in cubic structure within the *Im*$\overline{3}$ space group, in which the BO$_6$ octahedra are fairly rigid yet tilted substantially, transforming the originally twelve-fold coordinated *A*-site ions to square coordinated AO$_4$ units that are perpendicular to each other. In general, an antiferromagnetic (AFM) interaction is expected in between the *A*- and *B*-sites once the *B*-sites are filled with magnetic ions, as found in oxides such as CaCu$_3$Fe$_4$O$_{12}$ [1], BiCu$_3$Mn$_4$O$_{12}$ [2], LaCu$_3$Mn$_4$O$_{12}$ [3], and CaCu$_3$Mn$_4$O$_{12}$ [4]. On the other hand, when the *B*-site ion is non-magnetic, spins of *A*-site ions may contribute to the magnetic properties, making therefore a fundamental study

on the interplay of structure to magnetic properties extremely significant. One theory often used to predict and understand magnetic properties [10−15] is the Kramers−Anderson super-exchange, which addresses magnetic interaction between secondly closest cations via a non-magnetic anion. However, this theory is still case sensitive and the fundamental issue, namely, how magnetic elements actually interact in *A*-site ordered double perovskites, remains elusive. One typical example is the Cu-containing oxides, wherein CaCu$_3$Ti$_4$O$_{12}$ and CaCu$_3$Pt$_4$O$_{12}$, the extended Cu−O−Ti(Pt)−O−Cu superexchange induces an AFM nature, while in CaCu$_3$Ge$_4$O$_{12}$ and *A*′Cu$_3$Sn$_4$O$_{12}$ (*A*′ = Ca, Sr, and Pb), direct exchange (*i.e.*, coupling between nearest cations) gives rise to a ferromagnetic (FM) behavior [9,13,14].

The way of magnetic coupling remains a mystery particularly for the recently developed *A*-site ordered perovskite YMn$_3$Al$_4$O$_{12}$, which has high-spin Mn^{3+} at the *A*-site and non-magnetic Al^{3+} at the *B*-site [16]. It has been reported that this oxide is an AFM insulator arising possibly from the direct Mn−Mn exchange inter-action, which is quite opposite to the Cu-containing oxides, CaCu$_3$Ge$_4$O$_{12}$ and *A*′Cu$_3$Sn$_4$O$_{12}$ (*A*′ = Ca, Sr, and Pb) [13,14], being FM due to direct Cu−Cu exchange interaction, although they are analogs in chemistry: *A*-sites are filled with the Jahn−Teller ions (Mn vs. Cu) with a hole in *d* orbitals, whereas *B*-sites are

* Corresponding authors. Tel.: +86 431 85262030; fax: +86 431 85698041.
** Corresponding author. NANO Interface Technology Group, World Premier International Research Center, Advanced Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577. Tel.: +81 22 217 5933; fax: +81 22 217 5930.

E-mail addresses: lxjuan@ciac.jl.cn (X. Liu), zcwang@wpi-aimr.tohoku.ac.jp (Z. Wang), jmeng@ciac.jl.cn (J. Meng).

non-magnetic ions with no *d* orbitals (*e.g.*, Al vs. Sn). This clear deviation raises an appealing possibility that other mechanisms rather than the direct magnetic exchange may be responsible for the AFM state in $YMn_3Al_4O_{12}$, where its clarification may open an avenue for deepening understanding of magnetic coupling in *A*-site ordered double perovskites. Here, using first-principles calculations on $YMn_3Al_4O_{12}$, we demonstrate a qualitatively different type of magnetic coupling mode in *A*-site ordered double perovskites which can induce the AFM state, *i.e.*, extended (Mn–O)–(O–Mn) superexchange, and further identify the key factor that influences this superexchange by chemical substitutions. Such a mechanism differs from that addressed in the *A*-site ordered perovskite $YMn_3Sc_4O_{12}$, as presented in our previous work [17].

2. Computational details

All structures were optimized using the Vienna *ab initio* simulation package (VASP) under the framework of density-functional theory (DFT) [18]. We applied projector-augmented wave method [19] and the Perdew–Burke–Ernzerhof form of generalized gradient approximation (GGA) [20] with a $6 \times 6 \times 6$ *k*-point grid and a cutoff energy of 500 eV. All atoms were fully relaxed till magnitude of total energy and force fell below 1.0×10^{-6} eV and 1.0×10^{-3} eV/Å, respectively. Electronic structure calculations were performed applying the full-potential linearized augmented plane wave plus local orbitals method [21], which were implemented in WIEN2K package [22]. Wave function was expanded using the plane waves with a cutoff of 7.0 and the density and potential a value of 14. Brillouin zone integration was carried out with *k*-points of 1000 using the modified tetrahedron method [19]. Self consistence was achieved once total energy is converged to less than 10^{-5} Ry/f.u.

3. Results and discussion

It is known that $YMn_3Al_4O_{12}$ belongs to cubic $Im\overline{3}$ space group with a lattice constant of 7.180 Å, wherein *A′* and *A*-sites are ordered with a ratio of 1:3 and *B*-sites constitute heavily tilted AlO_6 octahedra [16] (Fig. 1). The calculated optimum lattice constant is
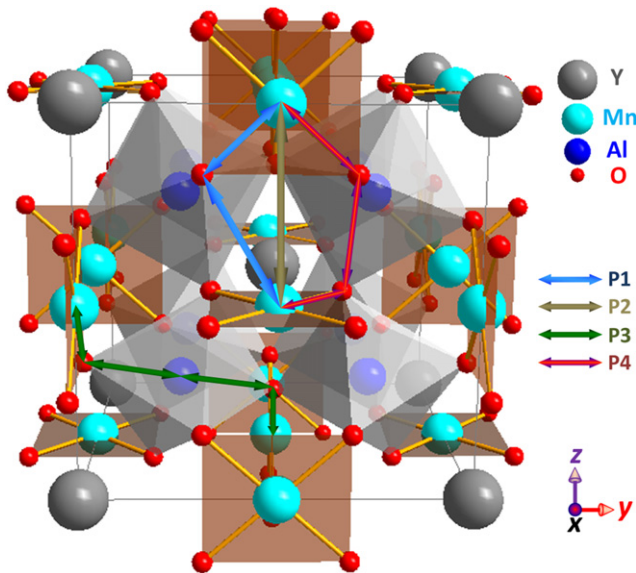
Table 1
The *A′*-site ionic radii (*r*), lattice constants (*a*), selected bond lengths in angstrom are listed below for $LaMn_3Al_4O_{12}$, $YMn_3Al_4O_{12}$, $LuMn_3Al_4O_{12}$, respectively, optimized (Opt.) by VASP, including the experimental (Exp.) structural parameters for $YMn_3Al_4O_{12}$ as a reference.

	$LaMn_3Al_4O_{12}$	$YMn_3Al_4O_{12}$		$LuMn_3Al_4O_{12}$
r	1.36	1.02		0.98
a	7.291	7.236 (Opt.)	7.180 (Exp.)	7.223
Mn–Mn	3.645	3.618	3.590	3.611
Mn–O	1.940	1.933	1.918	1.931
Al–O	1.932	1.917	1.901	1.913
O–O	2.713	2.721	2.693	2.723

7.236 Å and the length of Mn–Mn, Mn–O, Al–O, and O–O bonds is estimated to be 3.618, 1.933, 1.917, and 2.721 Å, respectively (listed in Table 1), very close to corresponding experimental values of 3.590, 1.918, 1.901, and 2.693 Å [16]. To determine magnetic ground state of $YMn_3Al_4O_{12}$, we have taken into account both FM and AFM arrangements of Mn^{3+} spins, and found that the latter is more stable by saving 176.4 meV/unit in energy, which agrees with the observed AFM state [16]. Fig. 2 shows the electronic structures of $YMn_3Al_4O_{12}$ with AFM state, calculated using energetically favored atomic geometry. Our calculations unambiguously reproduce the observed insulating nature with a band gap of ~2.0 eV. It is also clear that contribution to the bands around Fermi level (E_F) comes predominantly from Mn 3*d* and O 2*p* orbitals, namely, Y and Al atom contributions are negligible, which agrees with the previous report [16]. A significant issue that should be pointed out is that the partial density of states (PDOS) of Mn 3*d* and O 2*p* orbital are distributed within a very broad energy region, such as from about −7.0 eV to E_F, indicating the strong covalent hybridization interactions between them. Further analysis reveals that all spin-up orbitals of Mn are occupied except the $3d_{xz}$ component, while the spin-down orbitals are almost empty (Fig. 2(b)), indicating a d^4 configuration of high-spin Mn^{3+} state for the Mn. This is in line with X-ray absorption spectrum (XAS) of the Mn $L_{2,3}$-edges, where the spectral shape of $YMn_3Al_4O_{12}$ is quite similar to that of $La^{3+}Mn_3^{3+}Cr_4^{3+}O_{12}^{2-}$ with the Mn^{3+} at *A*-site [16]. Magnetic moment of Mn is estimated to be 3.4 μ_B and a small amount of magnetic moment is also present on the O, suggesting again the hybridization between them. These suggest that the charge combination is
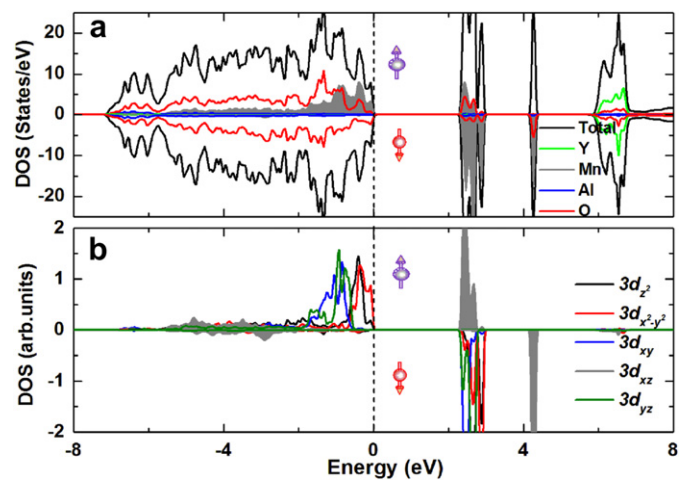

Fig. 1. (Color online) Four possible magnetic interaction paths in the $YMn_3Al_4O_{12}$: Mn–O–Mn superexchange (p1); direct Mn–Mn exchange (p2); Mn–O–Al–O–Mn superexchange (p3); and extended (Mn–O)–(O–Mn) superexchange (p4).

Fig. 2. (Color online) (a) Total DOS and PDOS plots of the Y, Mn, Al and O atom contributions for the AFM configuration of $YMn_3Al_4O_{12}$. (b) PDOS plots of the Mn 3*d* orbitals for the $YMn_3Al_4O_{12}$ with AFM state. The PDOS of the empty $3d_{xz}$ component is highlighted by shading. The Fermi level is aligned to zero and indicated by a vertical dashed line.