ABSTRACT

ZHANG, YUEMEI. Density Functional Analysis of the Spin Exchange Interaction and Spin-Orbit Coupling in some Magnetic Oxides of Transition-Metal Elements. (Under the direction of Prof. Mike H. Whangbo).

Transition-metal magnetic oxides containing unpaired spins have low-lying excited states with different spin moments and hence exhibit a variety of magnetic properties as a function of temperature. Analysis of the nature and strengths of the spin exchange interactions between localized spins provides essential information in understanding the magnetic properties of magnetic oxides. Although spin-orbit coupling (SOC) interaction is weak, it can play a crucial role in determining the magnetic properties of transition-metal oxides with unpaired spins. In our research we investigate the magnetic and electronic properties of magnetic materials based on transition-metal oxides by examining spin exchange interactions and SOC effect on the basis of first principles density functional theory calculations.

One of the consequences of SOC is uniaxial magnetism. It is important to note that the electronic structure required for uniaxial magnetism is also the condition leading to Jahn-Teller (JT) instability. To investigate the competition between uniaxial magnetism and JT instability, we examined the recently discovered multiferroic compound Ca$_3$CoMnO$_6$, and its analogues Ca$_3$CoMO$_6$ (M = Co, Rh, Ir) based on density functional calculations including on-site repulsion and SOC. Ca$_3$CoMnO$_6$ is found to undergo a Jahn-Teller distortion thereby losing uniaxial magnetism but retain substantial magnetic anisotropy. Our analysis of Ca$_3$CoMO$_6$ (M = Co, Rh, Ir) reveals that the magnetic and electronic properties of these oxides are governed by an intimate interplay between Jahn-Teller instability, uniaxial magnetism, spin arrangement, direct metal-metal bonding, and SOC.
Another outcome of SOC is multiferoicity. The magnetic structure and ferroelectric polarization of the layered triangular multiferroic antiferromagnet CuFeO$_2$ were examined on the basis of density functional calculations, and were compared with those of the isostructural analogue AgCrO$_2$. We explored why CuFeO$_2$ requires a magnetic field applied along the c-axis to adopt a helical spiral-spin structure but AgCrO$_2$ does not, and how the ferroelectric polarization of CuFeO$_2$ is related to the asymmetric electron density distribution induced by helical spiral-spin order and to the handedness of the helical spin rotation.

On the basis of density functional calculations, we evaluated the spin exchange interactions of the layered magnetic oxides YBaM$_2$O$_5$ (M = Mn, Fe, Co) by performing mapping analysis to find that their strong inter-slab spin exchange leads to a three-dimensional magnetic ordering at high temperature, and estimated the relative stabilities of the checkerboard and stripe charge order patterns of YBaM$_2$O$_5$ (M = Mn, Fe, Co) to find that the preference for the charge order pattern does not depend on the presence or absence of Jahn-Teller active ions.
DEDICATION

To my parents and my husband.

此论文献给我亲爱的父母，感谢您们的养育之恩及对我无私的爱与支持！
BIOGRAPHY

The author was born in Jinan, Shandong, China in 1982. She got her Bachelor’s degree majoring in Applied Chemistry and her Master’s degree in Physical Chemistry from Shandong University in 2003 and 2006, respectively. During her MS degree program in Shandong University, she studied the sensitivity of boron-doped carbon nanotubes for toxic gases on the basis of density functional theory calculations. Since fall 2006, she enrolled in North Carolina State University as a graduate student and worked in Dr. Mike H. Whangbo’s group studying interesting properties of magnetic solids.
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CHAPTER 1

Introduction

Discrete and extended solids containing unpaired spins have low-lying excited states with different spin moments and hence exhibit a variety of magnetic properties as a function of temperature. The energy states of a magnetic system are commonly described in terms of crystal field splitting, spin exchange interaction, and spin-orbit coupling. The nature and strengths of the spin exchange interactions between localized spins are essential in understanding the ordered magnetic structures of magnetic solids. Although spin-orbit coupling (SOC) interactions is weaker than crystal field splitting and spin exchange interactions, it can play a crucial role in determining the magnetic properties of compounds with unpaired spins. In our research we investigated the magnetic properties of several transition-metal oxides by examining spin exchange interactions and SOC effect on the basis of first principles density functional theory (DFT) calculations.

This chapter is organized as follows: Section 1 deals with spin exchange interactions and evaluation of spin exchange parameters by performing the energy mapping analysis. Section 2 briefly summarizes a couple of important aspects of solid state magnetic compounds that arise from SOC, namely, uniaxial magnetism and multiferroicity. Section 3 presents brief summary of the compounds investigated in this dissertation. Section 4 contains computational details. Section 5 provides the organization of this dissertation.
1. Spin exchange interactions

A magnetic solid has low-lying excited states. The typical energy scales in dealing with such energies are small; 1 meV = 11.6 K (in k_B units) = 8.06 cm\(^{-1}\), and \(\mu_B H \approx 5.8 \times 10^{-2}\) meV \(\approx 0.67\) K (in k_B units) at the magnetic field of 1 T. Thus, the excitation energies of a magnetic solid are generally described in terms of parameters, that is, by using a spin Hamiltonian \(\hat{H}^{\text{spin}}\),

\[
\hat{H}^{\text{spin}} = -\sum_{i<j} J_{ij} \hat{S}_i \cdot \hat{S}_j, \quad (1)
\]

which is defined as a sum of spin exchange interactions between adjacent spin sites i and j, \(-J_{ij} \hat{S}_i \cdot \hat{S}_j\), where \(\hat{S}_i\) and \(\hat{S}_j\) are the spin operators at the sites i and j, respectively, and \(J_{ij}\) is the associated spin exchange parameter. With the sign convention of Eq. 1, \(J_{ij}\) is antiferromagnetic (AFM) when \(J_{ij} < 0\), but is ferromagnetic (FM) when \(J_{ij} > 0\). This Hamiltonian expresses excitation energies of a magnetic solid in terms of a set of spin exchange parameters \(J_{ij}\). The geometrical pattern of these parameters (i.e., the spin lattice) determines the topology of the excitation energy spectrum.

1.1. Qualitative aspect

For a spin dimer made up of two equivalent spin sites with one electron per site, suppose that the two spin sites 1 and 2 are described by the magnetic orbitals \(\phi_1\) and \(\phi_2\), respectively. The interaction between \(\phi_1\) and \(\phi_2\) leads to the molecular levels \(\psi_1\) and \(\psi_2\) of the dimer separated by \(\Delta e\) in energy (Fig. 1.1). The allowed spin states of this spin dimer are the
singlet and triplet states with the energy difference between them as $\Delta E = E_S - E_T$. This energy spectrum is reproduced by the spin Hamiltonian,

$$\hat{H}_{\text{spin}} = -J \hat{S}_1 \cdot \hat{S}_2,$$  

(2)

if with $J = \Delta E$. When the spin sites 1 and 2 are described by the magnetic orbitals $\phi_1$ and $\phi_2$, respectively, then the $J$ parameter is written as\textsuperscript{1,2}

$$J = J_F + J_{AF} = 2K_{12} - \frac{\langle \Delta e \rangle^2}{U_{\text{eff}}}.$$  

(3)

The FM component $J_F$ is proportional to the exchange integral $K_{12}$, which increases with increasing the overlap density $\phi_1 \phi_2$. The AFM component $J_{AF}$ is proportional to $\langle \Delta e \rangle^2$ and is inversely proportional to the effective on-site repulsion $U_{\text{eff}}$. Since $\Delta e$ is proportional to the overlap integral $\langle \phi_1 | \phi_2 \rangle$, the magnitude of $J_{AF}$ increases with increasing $\langle \phi_1 | \phi_2 \rangle$. Therefore, a spin exchange becomes AFM when the overlap integral $\langle \phi_1 | \phi_2 \rangle$ is large and the overlap density $\phi_1 \phi_2$ is small, but becomes FM when the overlap integral $\langle \phi_1 | \phi_2 \rangle$ is small and the overlap density $\phi_1 \phi_2$ is large.

1.2. Quantitative evaluation by energy-mapping

Spin exchange parameters are quantitatively evaluated by performing the energy mapping analysis based on DFT+U calculations. Suppose one identifies a set of $N$ spin exchange paths to consider for a given magnetic solid. To evaluate the values of the associated spin exchange parameters $J_1, J_2, \ldots, J_N$, the energy-mapping method determines the electronic energies $E_{\text{elec}}$ of the $N+1$ ordered spin states (i.e., broken-symmetry states) $i =$
1, 2, …, N+1) by DFT+U calculations so as to obtain N relative energies $\Delta E_{\text{elec}}$. For these calculations, it is important to make sure that all ordered-spin states are magnetic insulating states. The total spin exchange energies $E_{\text{spin}}$ of the $N+1$ ordered spin states can be determined by using the spin Hamiltonian $\hat{H}_{\text{spin}}$ (Eq. 1) defined in terms of $J_1, J_2, \ldots, J_N$ (namely, $J_{ij} = J_1 - J_N$) so as to determine $N$ relative energies $\Delta E_{\text{spin}}$ expressed in terms of $N$ parameters $J_1 - J_N$. In writing the expression of the total spin exchange energy for an ordered spin state in terms of $J_1 - J_N$, we employ the energy expressions for the FM and AFM arrangements of a general spin dimer whose spin sites $i$ and $j$ possess $N_i$ and $N_j$ unpaired spins (hence, spins $S_i = N_i/2$ and $S_j = N_j/2$), respectively.\textsuperscript{3,4} Given $J_{ij}$ as the spin exchange parameter for this spin dimer, the FM and AFM arrangements of this spin dimer lead to the spin exchange energies

**FM arrangement:** $-N_i N_j J_{ij}/4 = -S_i S_j J_{ij}$

**AFM arrangement:** $+N_i N_j J_{ij}/4 = +S_i S_j J_{ij}$ \quad (4)

Thus, the total spin exchange energy of an ordered spin arrangement is obtained by summing up all pair-wise interactions. Then, by mapping the $N$ relative energies $\Delta E_{\text{elec}}$ onto the $N$ relative energies $\Delta E_{\text{spin}}$, we obtain the values of $J_1 - J_N$. In determining $N$ spin exchanges $J_1, J_2, \ldots, J_N$, one may employ more than $N+1$ ordered spin states, hence obtaining more than $N$ relative energies $\Delta E_{\text{elec}}$ and $\Delta E_{\text{spin}}$ for the mapping.\textsuperscript{1} In this case, the $N$ parameters $J_1 - J_N$ can be determined by performing least-squares fitting analysis. In comparing the relative strengths of spin exchange parameters $J_{ij}$ involving spin sites with different numbers of
unpaired spins, it is necessary to use the effective spin exchange parameters $J_{ij}^{\text{eff}}$ that incorporate the values of the associated spins $S_i$ and $S_j$, namely,

$$
J_{ij}^{\text{eff}} = S_i S_j J_{ij}
$$

The energy-mapping method described above is objective in that, once a set of spin exchange paths is chosen for a magnetic solid, it does not presume whether the associated spin exchange parameters should be FM or AFM. This method simply maps the electronic energy spectrum of DFT+U calculations onto the energy spectrum of the spin Hamiltonian defined by a set of spin exchange parameters. However, the values of the resulting spin exchange parameters depend on what set of exchange paths one selects. In identifying the spin lattice appropriate for a magnetic solid under consideration, therefore, energy-mapping analysis should be carried out for a set of spin exchange paths large enough to include all important ones. In particular, for magnetic solids consisting of both M-O-M and M-O…O-M spin exchange paths, those M-O…O-M paths with short O…O contact distances should not be omitted in the energy-mapping analysis.

When a set of spin exchange parameters are evaluated by performing DFT+U calculations as a function of on-site repulsion $U$, it is generally found that the values of AFM spin exchanges become smaller in magnitude with increasing $U$.\(^5\text{-}^7\) For magnetic systems with well localized electrons, for which increasing $U$ does not increase the moment on each spin site, this is expected because the AFM component $J_{\text{AF}}$ of a spin exchange decreases in strength with increasing the effective on-site repulsion $U^{\text{eff}}$, i.e., $J_{\text{AF}} = -(\Delta \epsilon)^2 / U^{\text{eff}}$. Given several sets of spin exchange parameters calculated for a magnetic solid from DFT+U
calculations with various \( U \) values, the relative strengths of the spin exchange parameters are not strongly affected by \( U \), hence predicting an identical spin lattice for the magnetic system. To check the proper range of \( U \) values, one may calculate the Curie-Weiss temperature \( \theta \) in the mean-field approximation, which is given by \(^8\)

\[
\theta = \frac{S(S+1)}{3k_B} \sum_i z_i J_i, \tag{6}
\]

where the summation runs over all nearest neighbors of a given spin site, \( z_i \) is the number of nearest neighbors connected by the spin exchange parameter \( J_i \), and \( S \) is the spin quantum number of each spin site.

2. Important consequences of spin-orbit coupling in magnetic solids

The SOC of a magnetic ion is discussed in terms of the Hamiltonian

\[
\hat{H}_{\text{SOC}} = \lambda \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \tag{7}
\]

where \( \lambda \) is the SOC constant of the ion, and \( \hat{\mathbf{L}} \) and \( \hat{\mathbf{S}} \) are the orbital and spin angular momentum operators of the magnetic ion, respectively. For a transition-metal ion with lower than \( d^5 \) electron count, \( \lambda > 0 \), so the orbital and spin moments couple antiparallel to each other to produce the lowest-energy angular momentum state \( J = -L + S \). For a transition-metal ion with higher than \( d^5 \) electron count, \( \lambda < 0 \), so the orbital and spin moments couple parallel to each other to produce the lowest-energy angular momentum state \( J = L + S \). For a high-spin \( d^5 \) metal ion, \( L = 0 \), to a first approximation (i.e., in the sense of free transition-metal ion), so the effect of SOC is expected to be weak.
2.1. Uniaxial magnetism

A magnetic system with uniaxial magnetism has a nonzero magnetic moment only along one direction in space.\textsuperscript{9,10} The consideration of the crystal field and SOC effects shows that, for a system with transition-metal magnetic ions to have uniaxial magnetic properties, the following three conditions should be satisfied:\textsuperscript{9}

(a) The site symmetry of the transition-metal ion should have an $n$-fold rotational symmetry with $n \geq 3$, so that its d-levels have degenerate sets, i.e., \{$(x^2-y^2, xy)$ and $(xz, yz)$ with the z-axis taken along the rotational axis.

(b) The d-electron count of the transition-metal ion should be such that one of the two degenerate d-states is occupied by three electrons, and hence the ground state of the ion is described by two degenerate electronic configurations with nonzero orbital angular momentum. As a representative example, \textbf{Fig. 1.2} shows the two degenerate electronic configurations of $(\text{Me}_3\text{Si})_3\text{C-Fe-C(SiMe}_3)_3$, in which the C-Fe-C frame is linear and the Fe atom exists as a high-spin Fe$^{2+}$ (d$^6$) ion.

(c) The d-states should be more than half filled so that the SOC constant is negative (\(\lambda < 0\)). Then, in the ground state arising from the SOC interaction $\lambda \vec{L} \cdot \vec{S}$, $\vec{L}$ and $\vec{S}$ become parallel to each other so that the $J = L + S$ value is large, and the $\Delta J_z$ values becomes greater than 1 (note that $J_z = \pm J$).

It is important to note that the electronic structure required for uniaxial magnetism is also the condition leading to Jahn-Teller (JT) instability. The latter refers to the tendency of a system with degenerate electronic states to undergo a geometrical distortion that removes the degeneracy of the electronic state.\textsuperscript{11} Thus, the JT distortion of a system with unaxial
magnetism will remove the n-fold \( (n \geq 3) \) rotational symmetry that is responsible for the uniaxial magnetism to begin with. In other words, uniaxial magnetism and JT instability are incompatible, unless JT distortion is prevented by steric hindrance as in \((\text{Me}_3\text{Si})_3\text{C-Fe-C(SiMe}_3)_3\).\(^\text{10}\) It is of interest to examine how these opposing factors compete in systems with no strong steric hindrance.

2.2. Multiferroicity

A magnetic solid might undergo a long-range magnetic order when the temperature is lowered. If the magnetic order removes the inversion symmetry of the lattice, the magnetic solid exhibits nonzero ferroelectric (FE) polarization.\(^\text{12-16}\) Such a magnetic system is known as a multiferroics. Experimentally, three types of magnetic order are known to remove the lattice inversion symmetry, namely, an up-up-down-down (\(\uparrow\uparrow\downarrow\downarrow\)) spin order in a 1D chain made up of two different magnetic ions alternating along the chain,\(^\text{17}\) a spiral spin order in a one-dimensional (1D) chain of identical magnetic ions,\(^\text{12-14,18-21}\) and helical spiral-spin order in the chains of metal (M) ions of the MO\(_2\) layers in the layered triangular antiferromagnets such as AgCrO\(_2\)\(^\text{22,23}\) and CuFeO\(_2\).\(^\text{24-26}\)

The spiral-spin order in a 1D chain of magnetic ions occurs when their spin exchange interactions are frustrated. Katsura, Nagaosa and Balatsky (KNB) showed that the FE polarization of a magnetic solid with spiral-spin order arises from the effect of SOC.\(^\text{27}\) In essence, the SOC induces mixing between the occupied and unoccupied magnetic states (obtained in the absence of SOC effects), and the electronic structure resulting from this
mixing loses the lattice inversion symmetry even if the ions of the lattice do not move from their centro-symmetric positions.\textsuperscript{27}

Suppose that $\vec{S}_i$ and $\vec{S}_j$ are the spin moments at the adjacent spin sites $i$ and $j$ of a 1D chain of magnetic ions, respectively, and $\vec{e}_{ij}$ is the vector connecting the two spin sites. Then, the FE polarization $\vec{P}_{ij}$ is related to $\vec{e}_{ij}$, $\vec{S}_i$ and $\vec{S}_j$ as\textsuperscript{27-29}

$$\vec{P}_{ij} \propto \vec{e}_{ij} \times \left( \vec{S}_i \times \vec{S}_j \right),$$

which is known as the KNB model. As depicted in \textbf{Fig. 1.3}, a 1D chain of spin moments might undergo one of the three kinds of spin order, i.e., cycloidal, sinusoidal or helical. According to the KNB model, only the cycloidal spin order leads to a nonzero FE polarization.

\textit{AgCrO$_2$} exhibits FE polarization ($\sim 5 \, \mu\text{C/m}^2$) in the magnetic ground state below $\sim 21$ K, in which each triangular spin lattice (TSL) of Cr$^{3+}$ ions separates into helical-spin chains of Cr$^{3+}$ ions.\textsuperscript{22,23} In the spiral-spin state of CuFeO$_2$ below $\sim 10$ K, the spins of each FeO$_2$ layer are separated into helical spiral-spin chains of Fe$^{3+}$ ions leading to FE polarization ($\sim 200 \, \mu\text{C/m}^2$).\textsuperscript{24-26} From the viewpoint of the KNB model, the finding in those layered triangular antiferromagnets is apparently puzzling. The FE polarization in AgCrO$_2$ and CuFeO$_2$ has been explained by noting that a magnetic structure with C$_2$ rotation symmetry leads to FE polarization along the rotation axis.\textsuperscript{30} Arima examined the possible directions of FE polarization in CuFeO$_2$ by analyzing the symmetry of the magnetic structure of an isolated FeO$_2$ layer composed of helical-spin chains,\textsuperscript{26} to find that the direction of FE polarization depends on the orientation of the screw-rotation plane. Seki \textit{et al.} presented a similar
discussion for the FE polarization of AgCrO\textsubscript{2}.\textsuperscript{23} It is of interest to investigate the FE polarization by electronic structure calculations to confirm the symmetry argument and find a more general rule for predicting the FE polarization of layered triangular antiferromagnets.

3. Magnetic oxides studied in this dissertation

To investigate the competition between uniaxial magnetism and JT instability, we examined the recently discovered multiferroic compound Ca\textsubscript{3}CoMnO\textsubscript{6},\textsuperscript{17} and its analogues Ca\textsubscript{3}CoMO\textsubscript{6} (M = Co,\textsuperscript{31} Rh,\textsuperscript{32} Ir\textsuperscript{33}) based on density functional analysis. The room-temperature crystal structure of Ca\textsubscript{3}CoMnO\textsubscript{6} has the 3-fold rotational symmetry,\textsuperscript{34} and its spins are regarded as Ising spins.\textsuperscript{17} The magnetic properties of Ca\textsubscript{3}CoMO\textsubscript{6} (M = Co, Rh, Ir) show that the Co atoms are present as high-spin ions,\textsuperscript{35} and the CoMO\textsubscript{6} chains have uniaxial spins. Thus, Ca\textsubscript{3}CoMnO\textsubscript{6} and its analogues Ca\textsubscript{3}CoMO\textsubscript{6} (M = Co, Rh, Ir) should be susceptible to JT instability. We carried out density functional theory calculations to examine how strong their JT distortions can be.

As discussed before, the triangular antiferromagnets AgCrO\textsubscript{2}\textsuperscript{23} and CuFeO\textsubscript{2}\textsuperscript{26} show FE polarization in their helical spiral-spin state, and the FE polarization was explained by symmetry argument.\textsuperscript{23,26,30} However, the symmetry analyses cannot predict whether the FE polarization should be pointed along the positive or negative direction of the rotational symmetry axis and how the polarization direction depends on the sense of the helical rotation (left- or right-handed rotation). This issue was investigated by performing density functional theory calculations.
Finally, the layered magnetic oxides YBaM$_2$O$_5$ (M = Mn, Fe, Co),$^{36-40}$ exhibiting charge, spin and orbital order of their transition-metal cations, were analyzed on the basis of density functional calculations. YBaMn$_2$O$_5$ exhibits a checkerboard charge order of the Mn$^{2+}$ and Mn$^{3+}$ ions,$^{36-38}$ whereas both YBaFe$_2$O$_5$$^{39}$ and YBaCo$_2$O$_5$$^{40}$ show a stripe charge order of the M$^{2+}$ and M$^{3+}$ (M = Fe, Co) ions with the stripes running along the b-direction. We evaluated the spin exchange interactions of YBaM$_2$O$_5$ (M = Mn, Fe, Co) by performing energy-mapping analysis based on density functional calculations and estimated the relative stabilities of the checkerboard and stripe charge order patterns of YBaM$_2$O$_5$ (M = Mn, Fe, Co) by optimizing their structures with density functional calculations to reproduce the observed charge order patterns.

4. Computational details

4.1. Density functional theory

Density functional theory (DFT) is applied to analyze the electronic structures in our work. In quantum mechanics,$^{41}$ the electronic structure of a many-electron system is described by the Schrödinger equation

$$\hat{H} \Psi(r, R) = E\Psi(r, R), \quad (9)$$

where $\hat{H}$ is Hamiltonian. In the Born-Oppenheimer approximation, the Hamiltonian is written as,$^{41}$

$$\hat{H}(r, R) = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} e^2 \left| r_i - r_j \right| - \sum_{\alpha} \sum_i \frac{Ze^2}{\left| r_i - R_{\alpha} \right|}, \quad (10)$$
which describe the electronic kinetic energy, electron-electron repulsion and electron-nuclear attraction. The main idea of DFT is to describe an interacting system of electrons via its electron density \( \rho \) instead of calculating its wave function. Hohenberg and Kohn\(^{42} \) proved that for a system with nondegenerate ground state, the ground-state energy \( E_0 \) is uniquely determined by the ground-state electron density \( \rho_0(x,y,z) \). The ground-state electronic energy \( E_0 \) is a function of \( \rho_0 \), namely, \( E_0 = E_0[\rho_0] \). According to the Hohenberg-Kohn theorem, the ground-state electronic wave function \( \psi_0 \) of an many-electron system is an eigenfunction of the purely electronic Hamiltonian \( \hat{\mathcal{H}} \),

\[
\hat{\mathcal{H}} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_i v_{\text{ext}}(r_i) + \frac{1}{2} \sum_{i<j} \frac{e^2}{|r_i - r_j|},
\]

where \( v_{\text{ext}}(r_i) \) is the external potential acting on the electron \( i \), and the energy \( E_0 \) is written as

\[
E_0 = E_v[\rho_0] = T[\rho_0] + V_{\text{Ne}}[\rho_0] + V_{\text{ee}}[\rho_0]
\]

\[
= \int \rho_0(\vec{r}) v(\vec{r}) \, d(\vec{r}) + T[\rho_0] + V_{\text{ee}}[\rho_0] = \int \rho_0(\vec{r}) v(\vec{r}) \, d(\vec{r}) + F[\rho_0],
\]

where the functional, \( F[\rho_0] = T[\rho_0] + V_{\text{ee}}[\rho_0] \), is independent of the external potential.

4.2. Exchange-correlation energy functionals

The major problem with DFT is that the exact expression of the exchange-correlation functional is not known except for the free electron gas. However, approximate expressions exist that permit the calculation of certain physical quantities quite accurately. In this article, the local spin density approximation (LSDA)\(^{42} \) and the generalized-gradient approximation
(GGA)$^{42}$ were used as the exchange-correlation functionals. In the LSDA, the functional depends only on the local density and is given by,$^{42}$

$$E_{xc}^{LSDA}[\rho] = \int \rho(\vec{r}) \in_{xc} (\rho(\alpha), \rho(\beta)) \, d(\vec{r}),$$  (13)

where the integral is over all space, $\in_{xc}(\rho)$ is the exchange plus correlation energy per electron in a homogeneous electron gas with electron density $\rho$, and $\alpha$ and $\beta$ represent up-spin and down-spin spins, respectively. The GGA depends on the local density and its gradient as,$^{42}$

$$E_{xc}^{GGA}[\rho^{\alpha}, \rho^{\beta}] = \int f(\rho^{\alpha}(\vec{r}), \rho^{\beta}(\vec{r}), \nabla \rho^{\alpha}(\vec{r}), \nabla \rho^{\alpha}(\vec{r})) \, d(\vec{r}).$$  (14)

4.3. Calculations of ferroelectric polarization

King-Smith and Vanderbilt$^{43}$ as well as Resta$^{44}$ showed that the electronic contribution to the FE polarization of a noncentrosymmetric system is associated with a geometric quantum phase (i.e., the Berry phase) of its valence wave functions. The values of FE polarizations in this article were calculated by using the Berry phase method$^{43,44}$ encoded in the Vienna \textit{ab initio} simulation package (VASP)$^{45}$

4.4. On-site repulsion $U$

For magnetic solids containing typically 3d transition metals, DFT calculations with LSDA or GGA invariably predict metallic electronic structures (i.e., electronic structure with partially filled bands) even if spin-polarized DFT calculations are performed. To remove this deficiency of DFT calculations, one typically employs the DFT plus on-site repulsion $U$ (i.e.
DFT+U) method,\textsuperscript{46,47} in which U of certain value is added to the transition metal atoms to ensure a large split between their up-spin and down-spin d-states so that the resulting electronic structure has a band gap. It is noted that DFT+U calculations are empirical because the choice of U is empirical. In our report, DFT+U calculations with LSDA and GGA are referred to as LSDA+U and GGA+U calculations, respectively. In addition, when these calculations include SOC effects\textsuperscript{48}, they are referred to as LSDA+U+SOC and GGA+U+SOC calculations, respectively.

4.5. Program packages employed

There are a number of program packages that allow one to perform DFT electronic structure calculations. In our work, the WIN2K\textsuperscript{49} and VASP\textsuperscript{45} codes were used to investigate the magnetic properties of transition metal oxides. The WIEN2k\textsuperscript{49} code (http://www.wien2k.at/), based on the full-potential linearized augmented plane-wave (FPLAW)+local orbital method, describes all electrons of a given system. In the VASP\textsuperscript{45} code (http://cms.mpi.univie.ac.at/vasp/), only the valence electrons of a given system are described by using the projector-augmented wave (PAW) method, and the interactions between ions and electrons by the ultrasoft Vanderbilt pseudopotentials.

5. Organization of the Dissertation

In the following the dissertation presents those papers already published in the literature and a paper submitted for publication. One paper that is under preparation is not included.
REFERENCES


Figure 1.1. Orbital interaction between two spin sites described by the magnetic orbitals $\phi_1$ and $\phi_2$ leading to the dimer levels $\psi_1$ and $\psi_2$ separated by the energy gap $\Delta e$.

Figure 1.2. (a) Two degenerate electron configurations of $(\text{Me}_3\text{Si})_3\text{C}-\text{Fe}-\text{C(}\text{SiMe}_3)_3$ containing a high-spin Fe$^{2+}$ ($d^6$) ion in the linear two-coordinate site. (b) Correspondence between the Cartesian and the spherical-harmonics representations for the split d-states of the linear-two coordinate Fe$^{2+}$ ($d^6$) ion.
Figure 1.3. Schematic illustration of three types of magnetic structures in a 1D chain of magnetic ions: (a) cycloidal, (b) sinusoidal, and (c) screw (or helical).
CHAPTER 2

Interplay between Jahn-Teller instability, uniaxial magnetism and ferroelectricity in Ca$_3$CoMnO$_6$

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Y. Zhang$^1$, H. J. Xiang$^2$ and M.-H. Whangbo$^1$

$^1$ Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204, USA

$^2$ National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401, USA

Abstract

Ca$_3$CoMnO$_6$ is composed of CoMnO$_6$ chains made up of face-sharing CoO$_6$ trigonal prisms and MnO$_6$ octahedra. The structural, magnetic, and ferroelectric properties of this compound were investigated on the basis of density-functional theory calculations. Ca$_3$CoMnO$_6$ is found to undergo a Jahn-Teller distortion associated with the CoO$_6$ trigonal prisms containing high-spin Co$^{2+}$ ($d^7$) ions, which removes the C$_3$ rotational symmetry and hence uniaxial magnetism. However, the Jahn-Teller distortion is not strong enough to fully quench the orbital moment of the high-spin Co$^{2+}$ ions thereby leading to an electronic state with substantial magnetic anisotropy. The Jahn-Teller distorted Ca$_3$CoMnO$_6$ in the magnetic ground state with up-up-down-down spin arrangement is predicted to have electric
polarization much larger than experimentally observed. Implications of the discrepancy between theory and experiment were discussed.

1. Introduction

Orbital ordering in transition-metal magnetic oxides arises when their transition-metal ions possess an electron configuration with unevenly filled degenerate $d$ states [e.g., three electrons in a doubly-degenerate $d$ state ($xy, x^2−y^2$) leading to the configuration ($xy, x^2−y^2)^3$] and hence Jahn-Teller (JT) instability. Such an electron configuration is also required for a transition-metal ion to have uniaxial magnetism, in which the ion has a nonzero orbital moment only along the axis of the rotational symmetry (conventionally taken to be the $z$ axis) leading to the degenerate $d$ states, so that the spins of the ion become Ising spins. Thus, uniaxial magnetism is incompatible with JT instability, unless a JT distortion is prevented so that the degenerate $d$ states remain. For example, the high-spin Fe$^{2+}$ ($d^6$) ion at the linear two-coordinate site of Fe[Cr(SiMe$_3$)$_3$]$_2$ has the $d$-electron configuration ($xy, x^2−y^2)^3(xz, yz)^2(z^2)^1$ (Refs. 2 and 3), so that Fe[Cr(SiMe$_3$)$_3$]$_2$ has JT instability but exhibits uniaxial magnetism because the sterically bulky C(SiMe$_3$)$_3$ groups prevent a JT distortion (i.e., the bending of the linear C-Fe-C framework). It is an open question what happens to uniaxial magnetism when a magnetic system with JT instability undergoes a weak JT distortion. This question is particularly relevant for the recently discovered multiferroic compound Ca$_3$CoMnO$_6$, whose room-temperature crystal structure has the 3-fold rotational symmetry, because its high-spin Co$^{2+}$ ($d^7$) ions at the trigonal prism sites have the electron configuration ($z^2)^3(xy, x^2−y^2)^3(xz, yz)^3$ and hence have JT instability (see below). At present, it is unknown whether or not...
Ca$_3$CoMnO$_6$ undergoes a JT distortion at a low temperature, but its spins are regarded as Ising spins. Thus, if a JT distortion takes place in Ca$_3$CoMnO$_6$, it will affect not only the magnetic anisotropy but also the ferroelectric (FE) polarization of Ca$_3$CoMnO$_6$.

In ferroelectrics driven by magnetism, the FE polarization arises from the loss of lattice inversion symmetry brought about by magnetic order. Experimentally, two types of magnetic order have been found to remove lattice inversion symmetry, namely, the spiral spin order in one-dimensional (1D) chains made up of identical magnetic ions and the up-up-down-down (↑↑↓↓) spin order in 1D chains made up of two different magnetic ions alternating along the chain. A number of magnetic oxides undergo spin spiral ordering and hence exhibit ferroelectricity. So far, the FE polarization induced by ↑↑↓↓ spin order in 1D chains is found in only one example, i.e., Ca$_3$CoMnO$_6$. Recently, it has been proposed that helical spin order can also induce FE polarization.

Ca$_3$CoMnO$_6$ consists of CoMnO$_6$ chains in which face-sharing CoO$_6$ trigonal prisms and MnO$_6$ octahedra alternate along the c direction with short Co-Mn distance (2.646 Å) [Figs. 2.1(a) and 2.1(b)], and the Ca atoms surrounding the CoMnO$_6$ chains cap the edges of the O$_3$ triangles and the O$_4$ rectangles of the CoO$_6$ trigonal prisms [Fig. 2.1c]. The magnetic-susceptibility study of Ca$_3$CoMnO$_6$ suggested that the MnO$_6$ octahedra and the CoO$_6$ trigonal prisms have high-spin Mn$^{4+}$ ($d^3$) and high spin Co$^{2+}$ ($d^7$) ions, respectively. In contrast, the neutron-diffraction study reported that the Co$^{2+}$ ($d^7$) ions are in a low spin state. On the basis of x-ray absorption spectroscopy and first-principles density-functional theory (DFT) calculations, Wu et al. showed unambiguously that the trigonal prism and octahedral sites of Ca$_3$CoMnO$_6$ are occupied by high-spin Co$^{2+}$ and high-spin Mn$^{4+}$ ions, respectively. On
lowering the temperature, Ca₃CoMnO₆ undergoes a long-range magnetic ordering at 16.5 K, below which the spins of each CoMnO₆ chain adopts the ↑↑↓↓ arrangement thereby leading to FE polarization. The spins of Ca₃CoMnO₆ are oriented parallel to the c direction (∥c), and the high-spin Co²⁺ ions possess a high orbital moment (μₗ = 1.7 μₜ) according to DFT calculations by Wu et al. These observations suggest that the Co²⁺ ions have uniaxial magnetism. The high-spin Co²⁺ (d⁷) ion at a trigonal prism site of Ca₃CoMnO₆ has the configuration (z²)²(xy, x²−y²)³(xz, yz)² (Ref. 2) and hence JT instability. Unlike the case of Fe[Fe(C(SiMe₃))₃]₂, however, the CoO₆ trigonal prisms of Ca₃CoMnO₆ are not surrounded by bulky groups (Fig. 2.1c) so that their CoO₆ trigonal prisms may undergo a JT distortion hence removing the threefold rotational symmetry and lifting the degeneracy of the (xy, x²−y²) and (xz, yz) levels. The latter in turn will remove uniaxial magnetism, although a substantial magnetic anisotropy may remain in the JT distorted structure if the extent of JT distortion is small. Experimentally, the FE polarization of Ca₃CoMnO₆ is found only along the c direction (i.e., P∥c ≈ 90 μC/m² at 2 K). However, a JT distortion may give rise to a nonzero FE polarization perpendicular to the c direction as well. In the following we probed these questions on the basis of DFT calculations.

2. Calculations

First-principles spin-polarized DFT calculations for Ca₃CoMnO₆ were performed using the projector augmented wave method encoded in the Vienna ab initio simulation package (VASP) (Ref. 15) with the local-density approximation (LDA). To properly describe
the electron correlation associated with the 3d states of Co and Mn, We used the LDA plus on-site repulsion $U$ (LDA+$U$) method of Dudarev et al.\textsuperscript{16} In addition, spin-orbit coupling (SOC) effects\textsuperscript{17} were considered by performing LDA+$U$+SOC calculations with the spins oriented parallel to the $c$ direction (hereafter the $//c$-spin orientation) and also perpendicular to the $c$ direction (hereafter the $\perp c$-spin orientation). Our LDA+$U$+SOC calculations were carried out with the energy criterion of $10^{-5}$ eV for self-consistency, the plane-wave cut-off energy of 400 eV, and a set of $3\times3\times3$ $k$ points for the irreducible wedge of the Brillouin zone. Our LDA+$U$+SOC calculations with higher-precision energy-convergence criterion (e.g., $10^{-8}$ eV for self-consistency) lead to the same results as obtained from the use of the energy-convergence criterion of $10^{-5}$ eV. In their study of Wu et al.\textsuperscript{14} carried out DFT+$U$+SOC calculations with the WIEN2K program package\textsuperscript{18} using the generalized gradient approximation (GGA) (Ref. 19) and the DFT+$U$ method of Anisimov et al.\textsuperscript{20} (with $U=5.0$ and 4.0 eV for Co and Mn, respectively, and $J=0.9$ eV for both Co and Mn). In the DFT+$U$ method of Ref. 16 employed in our work, the on-site repulsion $U$ represents the effective on-site repulsion, which corresponds to $U-J$ in the DFT+$U$ method of Ref. 20.

3. Results and discussion

A. Magnetic ground state

To confirm that the $\uparrow\uparrow\downarrow\downarrow$ state is the magnetic ground state, we consider four ordered spin states depicted in Fig. 2.1(d), namely, the $\uparrow\uparrow\downarrow\downarrow$ state, the antiferromagnetic state $\uparrow\downarrow\uparrow\downarrow$, the $\downarrow\uparrow\uparrow\uparrow$ state with identical spins at the Mn sites, and the ferromagnetic state $\uparrow\uparrow\uparrow\uparrow$. For simplicity, the interchain interactions are regarded as ferromagnetic. These states were
constructed using the experimental geometry determined at room temperature.\textsuperscript{5} Our LDA+$U+$SOC calculations for the experimental geometry of Ca$_3$CoMnO$_6$ using the VASP show that the $\uparrow\uparrow\downarrow\downarrow$ and $\uparrow\downarrow\uparrow\downarrow$ states are the two lowest-energy states for various values of $U$ on Co and Mn. In their GGA+$U+$SOC calculations for Ca$_3$CoMnO$_6$ using the WIEN2K package,\textsuperscript{18} Wu \textit{et al}.\textsuperscript{14} found that the state in which each CoMnO$_6$ chain has the $\uparrow\downarrow\uparrow\downarrow$ spin arrangement is more stable than the state in which CoMnO$_6$ chain has the $\uparrow\uparrow\downarrow\downarrow$ spin arrangement. This result is not consistent with the experimental finding that the magnetic ground state of Ca$_3$CoMnO$_6$ has the $\uparrow\uparrow\downarrow\downarrow$ spin arrangement in each CoMnO$_6$ chain.\textsuperscript{4} In the initial stage of our DFT study, we also faced the same problem.

Our systematic LDA+$U+$SOC calculations for the experimental structure of Ca$_3$CoMnO$_6$ using the VASP reveal that the $\uparrow\uparrow\downarrow\downarrow$ state becomes more stable than the $\uparrow\downarrow\uparrow\downarrow$ state only when small $U$ values are used for both Co and Mn ($U_{\text{Co}}$ and $U_{\text{Mn}}$, respectively), for example, $U_{\text{Co}}=U_{\text{Mn}}=1.1$ eV, as summarized in Table 2.1. Thus, in our further LDA+$U+$SOC calculations using the VASP, we chose $U_{\text{Co}}=U_{\text{Mn}}=1.1$ eV unless mentioned otherwise. Although small, these $U$ values lead to an insulating gap for all ordered spin states of Ca$_3$CoMnO$_6$ considered in our work (see below). Note that, in reproducing the magnetic properties of TbMnO$_3$, it was found necessary to use a small $U$ for Mn (i.e., 2.0 eV).\textsuperscript{10} It should be pointed out that our LDA+$U+$SOC calculations using the WIEN2K program package, in which all electrons are taken into consideration, a slightly large $U$ value (e.g., $U_{\text{Co}}=U_{\text{Mn}}=2.1$ eV) can reproduce the experimental finding that the $\uparrow\uparrow\downarrow\downarrow$ state is more stable than the $\uparrow\downarrow\uparrow\downarrow$ state.
B. Competition between uniaxial magnetism and Jahn-Teller instability

**Figure 2.2(a)** shows the plots of the partial density of states (PDOS) of the Co 3$d$ states in the ground state $\uparrow\uparrow\downarrow\downarrow$ obtained from LDA+$U$+SOC calculations for the experimental structure. The up-spin and down-spin $z^2$ states are both occupied. For each of the $xy$ and $x^2-y^2$ states, the up-spin state is occupied, while only one of the down-spin states (split due to SOC) is occupied. For each of the $xz$ and $yz$ states, the up-spin state is occupied but the down-spin state is not. Consequently, the electron configuration of each Co atom is best described as

$$(z^2\uparrow)^1(xy\uparrow, x^2-y^2\uparrow)^2(xz\uparrow, yz\uparrow)^2(z^2\downarrow)^1(xy\downarrow, x^2-y^2\downarrow)^1,$$

which corresponds to a high-spin Co$^{2+}$ ($d^7$) ion as anticipated. This configuration has three electrons in the doubly degenerate level, i.e., $(xy, x^2-y^2)^3$, so that the Co$^{2+}$ ions will lead to not only uniaxial magnetism$^2$ but also JT instability.

To see if Ca$_3$CoMnO$_6$ undergoes a JT distortion, the structure of Ca$_3$CoMnO$_6$ in each of the four ordered spin states was optimized by LDA+$U$+SOC calculations. In this optimization, the cell parameters were fixed to the experimental values, but the atom positions were allowed to relax. Our calculations give rise to two different optimized structures, namely, the optimized structure with high orbital moment on Co$^{2+}$ (i.e., $1.50 \mu_B$) and that with low orbital moment (i.e., $0.56 \mu_B$) on Co$^{2+}$ (hereafter referred to as the high-$\mu_L$ and low-$\mu_L$ optimized structures, respectively). Our analysis of the optimized structures show that the high-$\mu_L$ optimized structure keeps the threefold rotational symmetry, whereas the low-$\mu_L$ optimized structure does not.$^{21}$ The relative energies, in meV per formula unit (f.u.),
of the four ordered spin states determined from our LDA+$U$+SOC calculations with spins oriented along the c direction are summarized in Table 2.2, which shows that the $\uparrow\uparrow\downarrow\downarrow$ state is the ground state for both the experimental and the optimized structures. The energy of each state increases in the order, the experimental structure $>$ the high-$\mu_L$ optimized structure $>$ the low-$\mu_L$ optimized structure. Thus, for each state, the distortion toward the low-$\mu_L$ optimized structure is a JT distortion because it removes the C$_3$ rotational symmetry. As summarized in Table 2.3, this conclusion remains valid when large values of $U_{Co}$ and $U_{Mn}$ are used for LDA+$U$+SOC calculations.

In the $\uparrow\uparrow\downarrow\downarrow$ state the Co-Mn distance is 2.599 Å when the spins of the two sites are identical, and 2.693 Å otherwise. The atom displacements involved in the JT distortions in the $\uparrow\uparrow\downarrow\downarrow$ and $\uparrow\uparrow\uparrow\uparrow$ states, with respect to the experimental structure, are depicted in Fig. 2.3, where the largest atom movement is 0.064 Å. An important consequence of the JT distortion is that the orbital moment of the Co$^{2+}$ ion is reduced by a factor of approximately three (i.e., from 1.50 $\mu_B$ to 0.56 $\mu_B$) (Table 2.4). The orbital moment of the Co$^{2+}$ ion is nonzero, which indicates that the JT distortion is not strong enough to completely quench the orbital angular momentum of Co$^{2+}$. This can be seen from the PDOS plots of the Co $xy$ and $x^2-y^2$ states calculated for the $\uparrow\uparrow\downarrow\downarrow$ state of Ca$_3$CoMnO$_6$ using the optimized structure with Jahn-Teller distortion (i.e., without C$_3$ rotational symmetry) shown in Fig 2.2(b). Unlike the case of the experimental structure (with C$_3$ rotational symmetry) [Fig. 2.2 (a)], the two PDOS peaks for the $xy$ or the $x^2-y^2$ state are not identical for the optimized structure with
Jahn-Teller distortion (i.e., without $C_3$ rotational symmetry) [Fig. 2.2(b)]. However, the difference between the two PDOS peaks is not strong.

C. Magnetic anisotropy

In the presence of a JT distortion, Ca$_3$CoMnO$_6$ in the $↑↑↓↓$ state cannot have uniaxial magnetism due to the loss of the threefold rotational symmetry.$^2$ The observed magnetic anisotropy of Ca$_3$CoMnO$_6$ indicates that, in the $↑↑↓↓$ state of the JT-distorted structure, the spins still prefer to orient along the $c$ direction. To confirm this implication, we also carried out LDA+$U$+SOC calculations for the $↑↑↓↓$ state of the JT-distorted Ca$_3$CoMnO$_6$ with spins oriented perpendicular to the $c$ axis ($\perp c$). These calculations show that the $\perp c$-spin orientation is less stable than the $\parallel c$-spin orientation by 6.9 meV/f.u., and leads to a smaller orbital moment for Co$^{2+}$ than does the $\parallel c$-spin orientation (i.e., 0.16 vs. 0.56 $\mu_B$). Thus, the spins of Ca$_3$CoMnO$_6$ prefer to orient along the $c$ direction even in the JT distorted structure, which renders the observed anisotropic magnetic character to Ca$_3$CoMnO$_6$. Similarly, LDA+$U$+SOC calculations for the isostructural magnetic oxides Ca$_3$Co$_2$O$_6$ and Ca$_3$CoRhO$_6$, which have high-spin Co$^{3+}$ and Co$^{2+}$ ions at the trigonal prism sites, respectively, show that they undergo a JT distortion thereby losing uniaxial magnetism but their spins strongly prefer to orient along the $c$ axis.$^{22}$

D. Spin-exchange interactions

To see why the ground magnetic state of Ca$_3$CoMnO$_6$ is the $↑↑↓↓$ state, we analyze the three intra-chain spin exchange interactions, i.e., the superexchange (SE) interaction $J_{Co-}$.
Mn between the nearest-neighbor Co\(^{2+}\) and Mn\(^{4+}\) ions, the supersuperexchange (SSE) interaction \(J_{\text{Co-Co}}\) between the two adjacent Co\(^{2+}\) ions, and the SSE interaction \(J_{\text{Mn-Mn}}\) between the two adjacent Mn\(^{4+}\) ions. For a pair of spin sites interacting via the spin-exchange parameter \(J\), the spin exchange energy is given by \(-mnJ/4\), where \(m\) and \(n\) are the numbers of unpaired spins at the spin sites.\(^{23}\) For the high-spin Co\(^{2+}\) and Mn\(^{4+}\) sites of Ca\(_3\)CoMnO\(_6\), that \(m = n = 3\). Therefore, in terms of the Heisenberg spin Hamiltonian made up of the spin-exchange parameters \(J_{\text{Co-Mn}}, J_{\text{Co-Co}}\) and \(J_{\text{Mn-Mn}}\), the total spin-exchange energies per f.u. of the four ordered spin states in Fig. 2.1(c) are written as

\[
E^{↑↑↓↓} = (9/4)(−J_{\text{Mn-Mn}} − J_{\text{Co-Co}}),
\]

\[
E^{↑↓↑↓} = (9/4)(−2J_{\text{Co-Mn}} + J_{\text{Mn-Mn}} + J_{\text{Co-Co}}),
\]

\[
E^{↓↑↑↑} = (9/4)(J_{\text{Mn-Mn}} − J_{\text{Co-Co}}),
\]

\[
E^{↑↑↑↑} = (9/4)(2J_{\text{Co-Mn}} + J_{\text{Mn-Mn}} + J_{\text{Co-Co}}).
\]

By mapping the energy differences between the four states given in terms of the spin-exchange parameters onto the corresponding energy differences obtained from the LDA+\(U\)+SOC calculations (Table 2.2), we obtain the values of \(J_{\text{Co-Mn}}, J_{\text{Co-Co}}\) and \(J_{\text{Mn-Mn}}\) listed in Table 2.4. These parameters are all antiferromagnetic and hence are not in support of the assumption by Choi et al.\(^4\) that the SE interaction \(J_{\text{Co-Mn}}\) is ferromagnetic. The SE interaction \(J_{\text{Co-Mn}}\) is strongly antiferromagnetic due to the short Co-Mn distance, which allows direct metal-metal overlap. The three exchange parameters satisfy the condition, \(J_{\text{Mn-Mn}} + J_{\text{Co-Co}} > J_{\text{Co-Mn}}\), that makes the \(↑↑↓↓\) state more stable than the \(↑↓↑↓\) state.

The strengths of these interactions decrease in the order \(J_{\text{Mn-Mn}} > J_{\text{Co-Mn}} > J_{\text{Co-Co}}\). It is of interest to probe why the SSE interaction \(J_{\text{Mn-Mn}}\) is strong but the SSE interaction \(J_{\text{Co-Co}}\) is
weak. The Mn$^{4+} (d^3)$ ion at an octahedral site has the $(t_{2g})^3$ configuration, and each $t_{2g}$ orbital has the Mn 3$d$ orbital combined out-of-phase with the O 2$p$ orbitals and is contained in the MnO$_4$ equatorial plane [Fig. 2.4(a)].$^{24}$ As depicted in Fig. 2.4(b) and 4(c), the magnetic orbitals of two adjacent Mn$^{4+}$ sites can overlap well through their O 2$p$ orbitals thereby leading to a strong antiferromagnetic interaction.$^{24}$ The SSE interaction $J_{\text{Co-Co}}$ is not strong because the magnetic orbitals of two adjacent CoO$_6$ trigonal prisms [Fig. 2.4(d)] cannot effectively overlap through the intervening MnO$_6$ octahedron because the rectangular faces of the two CoO$_6$ trigonal prisms faces are farthest away from each other [Fig. 2.4(e)].

It is noted from Table 2.2 that the energy difference between the $\uparrow\uparrow\downarrow\downarrow$ and other states becomes larger after geometry optimization, consistent with the exchange striction mechanism for the ferroelectricity in Ca$_3$CoMnO$_6$. In particular, in the $\uparrow\uparrow\downarrow\downarrow$ state, the spin-up (spin-down) Co atom moves towards (away from) the spin-up Mn atom to break the inversion symmetry. These displacements of the Co atoms confirm those suggested by Choi et al.$^4$, who suggested that the bond between Mn and Co with opposite spins is elongated to minimize the exchange interaction energy. This suggestion is not consistent with the fact that $J_{\text{Co-Mn}}$ is antiferromagnetic rather than ferromagnetic. We attribute the displacements to the fact that direct metal-metal bonding is stronger between adjacent metal ions with identical spin than between adjacent metal ions with opposite spins.$^{25}$

E. Ferroelectric polarization

To estimate the effect of the JT distortion on the FE polarization of Ca$_3$CoMnO$_6$ in the $\uparrow\uparrow\downarrow\downarrow$ state, the electric polarizations for the optimized structures of Ca$_3$CoMnO$_6$ were
calculated using the Berry phase method. With this method, one calculates the difference in polarization, so it is necessary to consider the “paraelectric” state to be used as the reference. It is difficult to identify an insulating paraelectric state for Ca$_3$CoMnO$_6$. However, we note that there exist two JT-distorted structures with the same total energy but with opposite polarization with respect to the paraelectric state; one structure leads to the other when the Cartesian coordinate of each atom is inverted [i.e., $(x,y,z)\rightarrow(-x,-y,-z)$]. Then, the FE polarization of the JT-distorted ground state is taken as one half of the difference between the polarizations of the two JT-distorted structures.

For the high-$\mu_L$ optimized structure of Ca$_3$CoMnO$_6$ (i.e., the structure with C$_3$ rotational symmetry), the polarization along the $c$ direction is nonzero ($P_{//c} = 17700 \mu\text{C/m}^2$), but that perpendicular to the $c$-direction is zero ($P_{\perp c} = 0$). For the low-$\mu_L$ optimized structure of Ca$_3$CoMnO$_6$ (i.e., the structure without C$_3$ rotational symmetry), $P_{\perp c}$ is nonzero and is greater than $P_{//}$ (i.e., 16800 vs. 12500 $\mu\text{C/m}^2$). It should be pointed out that our LDA+$U$+SOC calculations implicitly assumed an FE arrangement of the \perp c electric polarizations of the CoMnO$_6$ chains; to reduce the computational task, our calculations for the $\uparrow\uparrow\downarrow\downarrow$ state of Ca$_3$CoMnO$_6$ assumed the ferromagnetic arrangement between the CoMnO$_6$ chains, which leads to the FE arrangement between the JT-distorted CoMnO$_6$ chains.

Compared with the values of FE polarization calculated for the multiferroics such as LiCuVO$_4$, LiCu$_2$O$_2$, and TbMnO$_3$ (Refs. 9-11) driven by spiral spin order, the calculated polarization for Ca$_3$CoMnO$_6$ is much larger than the experimental value ($P_{//c} \approx 90 \mu\text{C/m}^2$ and
and is only an order of magnitude smaller than the large polarization found for LuFe$_2$O$_4$,\textsuperscript{27} which is driven by charge order. For LiCuVO$_4$,\textsuperscript{9} LiCu$_2$O$_2$,\textsuperscript{9} and TbMnO$_3$,\textsuperscript{10,11} as well as LuFe$_2$O$_4$,\textsuperscript{27} the values of the polarization obtained from DFT+$U$+SOC calculations are in reasonable agreement with experiment. To account for the unusually large difference between theory and experiment found for the FE polarization of Ca$_3$CoMnO$_6$, we note that Ca$_3$CoMnO$_6$ is a quasi-one-dimension system in which the coupling between adjacent CoMnO$_6$ is weak. Therefore, it is possible that not all chains have the same direction of FE polarization even in a single crystal sample thereby forming many different domains of FE polarization. In such a case, the measurements of FE polarization will lead to a small nonzero $P_{//c}$ and a vanishing $P_{\perp c}$ due to the cancellation of the FE polarization from different domains. In our calculations, however, all chains are assumed to be in a FE arrangement (i.e., in a single FE domain).

4. Concluding remarks

In summary, the phenomena of JT instability, uniaxial magnetism and FE polarization are intimately related to each other in Ca$_3$CoMnO$_6$. At low temperature, Ca$_3$CoMnO$_6$ is predicted to undergo a JT distortion thereby losing uniaxial magnetism but retain substantial magnetic anisotropy with orbital moment 0.56 $\mu_B$ along the chain direction. It would be of interest to verify the occurrence of a JT-distortion in Ca$_3$CoMnO$_6$, which should be detectable by Raman spectroscopy. For the JT distorted Ca$_3$CoMnO$_6$ in the magnetic ground state with $\uparrow\uparrow\downarrow\downarrow$ spin order, our calculations predict a strong electric polarization, much
larger than experimentally observed. This discrepancy can be explained if a single-crystal sample consists of many different domains with opposite FE polarization.

Acknowledgments

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21. The high orbital moment found for the Co$^{2+}$ ion (i.e., 1.7 μB) by Wu et al. (Ref. 14) indicates that the structure of Ca$_3$CoMnO$_6$ employed for their WIEN2K calculations has the C$_3$ rotational symmetry.


Table 2.1. Energy difference $\Delta E$ between the $\uparrow\downarrow\uparrow\downarrow$ and the $\uparrow\uparrow\downarrow\downarrow$ states of Ca$_3$CoMnO$_6$, $\Delta E = E_{\uparrow\uparrow\downarrow\downarrow} - E_{\uparrow\downarrow\uparrow\downarrow}$, obtained from LDA+$U+\text{SOC}$ calculations as a function of the on-site repulsions on the Mn and Co atoms ($U_{\text{Mn}}$ and $U_{\text{Co}}$, respectively).

<table>
<thead>
<tr>
<th>$U_{\text{Mn}}$ (in eV)</th>
<th>$U_{\text{Co}}$ (in eV)</th>
<th>$\Delta E$ (meV/f.u.)</th>
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<tr>
<td>1.1</td>
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<td>6.1</td>
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</tr>
<tr>
<td>6.1</td>
<td>4.1</td>
<td>30.7</td>
</tr>
</tbody>
</table>

Table 2.2. Relative energies (in meV/f.u.) of the four ordered spin states of Ca$_3$CoMnO$_6$ determined from LDA+$U+\text{SOC}$ calculations $U_{\text{Mn}}=U_{\text{Co}}=1.1$ eV

<table>
<thead>
<tr>
<th>Structure used</th>
<th>$\uparrow\uparrow\downarrow\downarrow$</th>
<th>$\uparrow\downarrow\uparrow\downarrow$</th>
<th>$\downarrow\uparrow\uparrow\uparrow$</th>
<th>$\uparrow\uparrow\uparrow\uparrow$</th>
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<tr>
<td>Experimental</td>
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<td>9.41</td>
<td>31.75</td>
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<td>Optimized with high $\mu_L$</td>
<td>0.00 (31.3)$^a$</td>
<td>14.38</td>
<td>21.87</td>
<td>53.12</td>
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<tr>
<td>Optimized with low $\mu_L$</td>
<td>0.00 (0.00)$^a$</td>
<td>11.89</td>
<td>21.26</td>
<td>52.93</td>
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</table>

$^a$ The numbers in the parentheses refer to the relative total energy (in meV) of the $\uparrow\uparrow\downarrow\downarrow$ state with respect to the energy of the optimized structure without $C_3$ symmetry.
Table 2.3. Relative energies (in meV/f.u.) of the ↑↓↑↓ and ↑↑↓↓ states of Ca$_3$CoMnO$_6$ determined from LDA+$U$+SOC calculations with $U_{\text{Mn}}=U_{\text{Co}}=2.1$ and 4.1 eV

<table>
<thead>
<tr>
<th>Structure used</th>
<th>$U_{\text{Mn}}=U_{\text{Co}}=2.1$ eV</th>
<th>$U_{\text{Mn}}=U_{\text{Co}}=4.1$ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>↑↑↓↓</td>
<td>↑↓↑↓</td>
</tr>
<tr>
<td>Experimental</td>
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<td>-4.20</td>
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$^a$ The numbers in the parentheses refer to the relative total energy (in meV) of the ↑↑↓↓ state with respect to the energy of the optimized structure without C$_3$ symmetry.
Table 2.4. Spin and orbital moments of the Co$^{2+}$ and Mn$^{4+}$ ions of Ca$_3$CoMnO$_6$ in the ↑↑↓↓ state determined from LDA+U+SOC calculations with $U_{\text{Mn}} = U_{\text{Co}} = 1.1, 2.1$ and $4.1$ eV

<table>
<thead>
<tr>
<th>Geometry used</th>
<th>Spin Moment</th>
<th>Orbital Moment $^a$</th>
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<td>Experimental $^b$</td>
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<td>2.93</td>
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$^a$ The positive and negative orbital moments mean that they are in the same and opposite directions to the spin moments, respectively.

$^b$ The results for $U_{\text{Mn}}=U_{\text{Co}}=1.1$ eV are given in the first row, those for $U_{\text{Mn}}=U_{\text{Co}}=2.1$ eV in the second row, and those for $U_{\text{Mn}}=U_{\text{Co}}=4.1$ eV in the third row.
Table 2.5. Spin-exchange parameters (in meV) of Ca₃CoMnO₆ extracted from LDA+U+SOC calculations with \( U_{\text{Mn}}=U_{\text{Co}}=1.1 \) eV

<table>
<thead>
<tr>
<th>Geometry used</th>
<th>( J_{\text{Co-Mn}} )</th>
<th>( J_{\text{Mn-Mn}} )</th>
<th>( J_{\text{Co-Co}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>3.34</td>
<td>2.09</td>
<td>1.63</td>
</tr>
<tr>
<td>Optimized with high ( \mu_L )</td>
<td>4.31</td>
<td>4.86</td>
<td>2.64</td>
</tr>
<tr>
<td>Optimized with low ( \mu_L )</td>
<td>4.56</td>
<td>4.72</td>
<td>2.47</td>
</tr>
</tbody>
</table>
Figure 2.1. (Color online) (a) Projection view of the crystal structure of Ca$_3$CoMnO$_6$ along the $c$ direction. (b) Perspective view of an isolated CoMnO$_6$ chain. (c) Arrangement of nine Ca atoms surrounding one CoO$_6$ trigonal prism, in which the edges of the O$_3$ triangles and the O$_4$ rectangles are capped by Ca. (d) Four-ordered spin arrangements of a single CoMnO$_6$ chain, where the large and small circles represent the Co$^{2+}$ and Mn$^{4+}$ ions, respectively, and the up and down spins are represented by the absence and presence of shading, respectively.
Figure 2.2. (Color online) (a) PDOS plots of the Co 3$d$ states calculated for the $\uparrow\uparrow\downarrow\downarrow$ state of Ca$_3$CoMnO$_6$ using the experimental structure, which has the C$_3$ rotational symmetry. The PDOS plots for the $xy$ and $x^2\!-\!y^2$ states are identical and so are those of the $xz$ and $yz$ states. (b) PDOS plots of the Co 3$d$ states calculated for the $\uparrow\uparrow\downarrow\downarrow$ state of Ca$_3$CoMnO$_6$ using the optimized structure with Jahn-Teller distortion (i.e., without C$_3$ rotational symmetry). For simplicity, only the PDOS plots for the $xy$ and $x^2\!-\!y^2$ states are shown. The energy on the horizontal axis is in units of eV, and the PDOS on the vertical axis in units of states/eV per Co atom (the positive and negative scale indicates the up-spin and down-spin states, respectively).
Figure 2.3. (Color online) Displacements of the atoms associated with the Jahn-Teller distortions in the (a) $↑↑↓↓$ and (b) $↑↑↑↑$ states of Ca$_3$CoMnO$_6$ with respect to their positions of the experimental structure.
Figure 2.4. (Color online) (a) Magnetic orbital contained in one MnO$_4$ equatorial plane of an isolated MnO$_6$ octahedron. (b) MnO$_4$ equatorial planes of two adjacent MnO$_6$ octahedra sharing one face of the intervening CoO$_6$ trigonal prism. (c) Projection view of the two magnetic orbitals associated with the two MnO$_4$ equatorial planes in (b). (d) Magnetic orbital of an isolated CoO$_6$ trigonal prism. (e) Rectangular faces of two adjacent CoO$_6$ trigonal prisms sharing an equatorial plane of the intervening MnO$_6$ octahedron.
CHAPTER 3

Density functional theory analysis of the interplay between Jahn-Teller instability, uniaxial magnetism, spin arrangement, metal-metal interaction and spin-orbit coupling in Ca$_3$CoMO$_6$ (M = Co, Rh, Ir)

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Yuemei Zhang$^1$, Erjun Kan$^1$, Hongjun Xiang$^2$, Antoine Villesuzanne$^3$

and Myung-Hwan Whangbo$^{1,*}$

$^1$ Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204, USA

$^2$ Key Laboratory of Computational Physical Sciences (Ministry of Education) and Department of Physics, Fudan University, Shanghai 200433, P. R. China

$^3$ CNRS, Université de Bordeaux, ICMCB, 87 Av. Dr. A. Schweitzer, 33608 Pessac cedex, France
Abstract

In the isostructural oxides Ca$_3$CoMO$_6$ (M = Co, Rh, Ir), the CoMO$_6$ chains made up of face-sharing CoO$_6$ trigonal prisms and MO$_6$ octahedra are separated by Ca atoms. We analyzed the magnetic and electronic properties of these oxides on the basis of density functional theory calculations including on-site repulsion and spin-orbit coupling, and examined the essential one-electron pictures hidden behind results of these calculations. Our analysis reveals an intimate interplay between Jahn-Teller instability, uniaxial magnetism, spin arrangement, metal-metal interaction, and spin-orbit coupling in governing the magnetic and electronic properties of these oxides. These oxides undergo a Jahn-Teller distortion but their distortions are weak, so that their trigonal-prism Co$^{n+}$ ($n = 2, 3$) ions still give rise to strong easy-axis anisotropy along the chain direction. As for the d-state split pattern of these ions, the electronic and magnetic properties of Ca$_3$CoMO$_6$ (M = Co, Rh, Ir) are consistent with $d_0 < (d_2, d_{-2}) < (d_1, d_{-1})$, but not with $(d_2, d_{-2}) < d_0 < (d_1, d_{-1})$. The trigonal-prism Co$^{3+}$ ion in Ca$_3$Co$_2$O$_6$ has the $L = 2$ configuration $(d_0)^1(d_2, d_{-2})^3(d_1, d_{-1})^2$ because of the metal-metal interaction between adjacent Co$^{3+}$ ions in each Co$_2$O$_6$ chain, which is mediated by their $z^2$ orbitals, and the spin-orbit coupling of the trigonal-prism Co$^{3+}$ ion. The spins in each CoMO$_6$ chain of Ca$_3$CoMO$_6$ prefer the ferromagnetic arrangement for M = Co and Rh, but the antiferromagnetic arrangement for M = Ir. The octahedral M$^{4+}$ ion of Ca$_3$CoMO$_6$ has the $(1a)^1(1e)^4$ configuration for M = Rh but the $(1a)^2(1e)^3$ configuration for M = Ir, which arises from the difference in the spin-orbit coupling of the M$^{4+}$ ions and the Co…M metal-metal interactions.

mike_whangbo@ncsu.edu
1. Introduction

For a magnetic system with transition-metal ions exhibiting uniaxial (i.e., Ising) magnetism, the ions have an unevenly filled degenerate d-states so that the $\Delta J_z$ value of the lowest-lying Kramer’s doublet state is greater than 1. However, such a system has Jahn-Teller (JT) instability and the associated JT distortion may lift the d-state degeneracy causing the uniaxial magnetism. Thus, a true uniaxial magnetism is not possible unless a JT distortion is prevented by steric hindrance. Indeed, uniaxial magnetism and JT instability were found to compete in the magnetic oxide $\text{Ca}_3\text{CoMnO}_6$, which consists of the $\text{CoMnO}_6$ chains made up of face-sharing $\text{CoO}_6$ trigonal prism (TP) and $\text{MnO}_6$ octahedron (OCT) units (Fig. 3.1). In the room-temperature structure of $\text{Ca}_3\text{CoMnO}_6$, each $\text{CoMnO}_6$ chain has a three-fold rotational symmetry, $C_3$, so that the high-spin $\text{Co}^{2+}$ ($d^7$) ion at each TP $\text{CoO}_6$ has the d-electron configuration $(d_0)^2(d_2, d_{-2})^3(d_1, d_{-1})^2$, giving rise to both JT instability and uniaxial magnetism. Here we use the local coordinate system in which the z-axis is taken along the $\text{CoMnO}_6$ chain (i.e., the crystallographic c-direction), so that the $d_0$ orbital is equivalent to the $z^2$ orbital, the degenerate $(d_2, d_{-2})$ set to the $(x^2-y^2, xy)$ set, and the degenerate $(d_1, d_{-1})$ set to the $(xz, yz)$ set (Fig. 3.2a). $\text{Ca}_3\text{CoMnO}_6$ is regarded to have uniaxial spins, but first principles density functional theory (DFT) calculations showed that $\text{Ca}_3\text{CoMnO}_6$ should undergo a JT distortion removing the $C_3$ symmetry and hence cannot be truly uniaxial, although it has strong magnetic anisotropy with the easy axis along the $\text{CoMnO}_6$ chain.
The magnetic oxides Ca$_3$CoMO$_6$ (M = Co, Rh, Ir), isostructural with Ca$_3$CoMnO$_6$, belongs to the family of hexagonal perovskites. Due to the face sharing of the TP CoO$_6$ and OCT MO$_6$, the nearest-neighbor (NN) Co…M distance of the CoMO$_6$ chain is short (i.e., 2.595, 2.682 and 2.706 Å for M = Co, Rh and Ir, respectively) so that the Co…M direct metal-metal interaction mediated by their z$^2$ orbitals can be substantial. (Here the NN Co…Ir distance of 2.706 Å is taken from the structure of Ca$_3$CoIrO$_6$ optimized by DFT calculations. See below.) The X-ray photoemission study of Ca$_3$CoMO$_6$ revealed that the Co atoms of the TP CoO$_6$ exist as Co$^{3+}$ ions for M = Co but as Co$^{2+}$ ions for M = Rh and Ir, and hence the M atoms of the MO$_6$ octahedra exist as M$^{3+}$ ions for M = Co but as M$^{4+}$ ions for M = Rh and Ir. The magnetic properties of Ca$_3$CoMO$_6$ (M = Co, Rh, Ir) show that the TP Co atoms are present as high-spin ions, the CoMO$_6$ chains have uniaxial spins, and their intrachain spin arrangement is ferromagnetic (FM) for M = Co and Rh, and the same is presumed to be true for M = Ir. The electronic and magnetic properties of Ca$_3$CoMO$_6$ (M = Co, Rh, Ir) have been investigated in a number of DFT studies.

It has been well established that the d-states of a transition metal ion at an isolated TP site with C$_3$ rotational symmetry are split as $d_0 < (d_2, d_{-2}) < (d_1, d_{-1})$. This leads to L = 0 configuration $(d_0)^2(d_2, d_{-2})^2(d_1, d_{-1})^2$ (Fig. 3.3a) for an isolated TP high-spin Co$^{3+}$ (d$^6$) ion, hence predicting the absence of uniaxial magnetism. Thus, it was concluded that the TP Co$^{3+}$ ion of Ca$_3$Co$_2$O$_6$ should have the L = 2 configuration $(d_0)^1(d_2, d_{-2})^3(d_1, d_{-1})^2$ (Fig. 3.3b) due to the interaction between the z$^2$ orbitals of adjacent TP and OCT Co$^{3+}$ ions. In the DFT study of Ca$_3$Co$_2$O$_6$ by Wu et al., spin-orbit coupling (SOC) interactions were found essential for the occurrence of the L = 2 configuration $(d_0)^1(d_2, d_{-2})^3(d_1, d_{-1})^2$; the TP Co$^{3+}$ ion
has the \((d_0)^1(d_{2}, d_{-2})^3(d_{1}, d_{-1})^2\) configuration if SOC interactions are included, but the \((d_0)^3(d_{2}, d_{-2})^2(d_{1}, d_{-1})^2\) configuration otherwise. Nevertheless, they assumed the split pattern of the TP Co\(^{3+}\) ion to be \((d_2, d_{-2}) < d_0 < (d_1, d_{-1})\), which leads to the \(L = 2\) configuration \((d_2, d_{-2})^3(d_0)^1(d_{1}, d_{-1})^2\) (Fig. 3.3c) even if the SOC effect is not included. Furthermore, Burnus et al.\(^{27}\) employed this \(L = 2\) configuration for the TP Co\(^{3+}\) ion to interpret their X-ray absorption and X-ray magnetic dichroism data of Ca\(_3\)Co\(_2\)O\(_6\), and concluded that the \(d_0 < (d_2, d_{-2}) < (d_1, d_{-1})\) pattern is incorrect for the TP Co\(^{3+}\) ion. However, the \((d_2, d_{-2}) < d_0 < (d_1, d_{-1})\) split pattern gives rise to serious conceptual difficulties. First, for a transition metal atom surrounded by oxygen ligands, the split pattern of its the d-states is determined by how strong the antibonding interactions between the metal nd and O 2p orbitals are.\(^{28}\) The \(z^2\) orbital of the TP Co\(^{3+}\) ion, being aligned along the C\(_3\) axis of the TP CoO\(_6\), overlaps least well with the 2p-orbitals of the surrounding O atoms. As a consequence, the \(d_0\) level should be the lowest-lying state of the TP Co d-states (Fig. 3.2a) regardless of whether the TP ion is Co\(^{3+}\) or Co\(^{2+}\), so that the \((d_2, d_{-2}) < d_0 < (d_1, d_{-1})\) split pattern cannot be correct. Second, the \((d_2, d_{-2}) < d_0 < (d_1, d_{-1})\) split pattern cannot explain the uniaxial magnetism of Ca\(_3\)CoRhO\(_6\), because it gives rise to the \(L = 0\) configuration \((d_2, d_{-2})^4(d_0)^1(d_{1}, d_{-1})^2\) for the TP Co\(^{2+}\) (d\(^7\)) ion (Fig. 3.3d). In contrast, the \(d_0 < (d_2, d_{-2}) < (d_1, d_{-1})\) split pattern gives the \(L = 2\) configuration \((d_0)^2(d_{2}, d_{-2})^3(d_{1}, d_{-1})^2\) (Fig. 3.3e), and the latter is consistent with the density functional calculations for Ca\(_3\)CoRhO\(_6\) by Wu et al.\(^{25}\) In interpreting their X-ray absorption and X-ray magnetic dichroism data of Ca\(_3\)CoRhO\(_6\), Burnus et al.\(^{29}\) used the \(d_0 < (d_2, d_{-2}) < (d_1, d_{-1})\) pattern for the TP Co\(^{2+}\) ion and suggested that the \(d_0\) state is nearly degenerate with the \((d_2, d_{-2})\) states.
The above discussion raises several important questions: (a) It is necessary to
determine whether or not the spins of the CoIrO$_6$ chains in Ca$_3$CoIrO$_6$ have the FM
arrangement as found in Ca$_3$Co$_2$O$_6$ and Ca$_3$CoRhO$_6$. (b) In all three oxides Ca$_3$CoMO$_6$ (M =
Co, Rh, Ir), the TP Co$^{n+}$ (n = 2 or 3) ions possess the L = 2 electron configuration. Thus,
Ca$_3$CoMO$_6$ (M = Co, Rh, Ir) should be susceptible to JT instability as found for
Ca$_3$CoMnO$_6$.\textsuperscript{4} It is important to examine how strong their JT distortions can be. (c)
Concerning the d-state split pattern of a transition-metal ion at a TP site, it is controversial
whether the d$_0$ < (d$_2$, d$_{-2}$) < (d$_1$, d$_{-1}$) or (d$_2$, d$_{-2}$) < d$_0$ < (d$_1$, d$_{-1}$) pattern is correct. It is desirable
to determine if the split pattern depends on the charge of the TP Co$^{n+}$ (n = 2, 3) ion as
reported in the studies of Burnus \textit{et al.}\textsuperscript{27,29} and/or whether the d$_0$ state is nearly degenerate
with the (d$_2$, d$_{-2}$) states as suggested by Burnus \textit{et al.}\textsuperscript{29} (d) In Ca$_3$CoMO$_6$ (M = Rh, Ir), the
OCT M$^{4+}$ ions might exhibit SOC effects because of their open-shell electron configuration
(t$_{2g}$)$^5$. It is interesting to examine if the SOC effects of these ions affect the electronic and
magnetic structures of Ca$_3$CoMO$_6$. In the present work, we investigate these questions on the
basis of DFT calculations for Ca$_3$CoMnO$_6$ (M = Co, Rh, Ir). Results of our study are
presented in what follows.

2. Calculations

To optimize the crystal structures of Ca$_3$CoMO$_6$ (M = Co, Rh, Ir) in the presence and
absence of $C_3$ rotational symmetry, we employed the projector augmented wave (PAW)
method encoded in the Vienna ab initio simulation package (VASP)\textsuperscript{30} with the local spin
density approximation (LSDA). To properly describe the electron correlation associated with
the d states of transition metal atoms, the LSDA plus on-site repulsion U (LSDA+U) method was adopted.\textsuperscript{31} In addition, SOC effects\textsuperscript{32} were considered by performing LSDA+U+SOC calculations with the spins oriented parallel and perpendicular to the CoMO\textsubscript{6} chain direction (hereafter the $//c$- and $\perp c$-spin orientations, respectively). The convergence threshold for our LSDA+U+SOC calculations was set to $10^{-5}$ eV in energy and $10^{-2}$ eV/Å in force with the plane-wave cutoff energy of 400 eV and a set of $3\times3\times3$ k-points for the irreducible Brillouin zone. For Ca\textsubscript{3}CoIrO\textsubscript{6}, only the cell parameters have been reported.\textsuperscript{33} Therefore, we determined the atomic positions of Ca\textsubscript{3}CoIrO\textsubscript{6} by optimizing the crystal structure on the basis of LSDA+U+SOC calculations. This optimization leads to two kinds of structures for each Ca\textsubscript{3}CoMO\textsubscript{6} ($M = \text{Co, Rh, Ir}$), namely, one with high orbital moment ($\mu_L$), and the other with low $\mu_L$, on the TP Co$^{n+}$ ($n = 2, 3$) ions. As found for Ca\textsubscript{3}CoMnO\textsubscript{6},\textsuperscript{4} the CoMO\textsubscript{6} chains of Ca\textsubscript{3}CoMO\textsubscript{6} have the $C_3$-rotational symmetry in the high-$\mu_L$ structure, but do not in the low-$\mu_L$ structure. The geometry optimization with LSDA+U+SOC calculations is carried out with no symmetry constraint, so it is generally difficult to have the calculations converge to the high-$\mu_L$ structure.

In discussing the spin and orbital moments of the TP and OCT ions of Ca\textsubscript{3}CoMO\textsubscript{6} ($M = \text{Co, Rh, Ir}$) as well as their density of states (DOS), we have carried out LSDA+U+SOC calculations for the experimental and the optimized structures of Ca\textsubscript{3}CoO\textsubscript{6} and Ca\textsubscript{3}CoRhO\textsubscript{6} and for the optimized structure of Ca\textsubscript{3}CoIrO\textsubscript{6} by using the full-potential linearized augmented plane wave (FPLAPW) method\textsuperscript{34} encoded in the WIEN2k package,\textsuperscript{35} $5\times5\times5$ k-points for the irreducible Brillouin zone, the threshold of $10^{-5}$ Ry for the energy convergence, the cut-off
energy parameters of $R K_{\text{max}} = 7$ and $G_{\text{max}} = 12$, and the energy threshold of $-9.0 \text{ Ry}$ for the separation of the core and valence states.

For the effective on-site repulsion $U_{\text{eff}} = U - J$ (where $J$ is the Stoner intra-atomic parameter) needed for the geometry optimization with the LSDA+$U$+SOC (VASP) calculations, we used $U_{\text{eff}} = 4 \text{ eV}$ on Co for $\text{Ca}_3\text{Co}_2\text{O}_6$, $U_{\text{eff}} = 4 \text{ eV}$ on Co and $U_{\text{eff}} = 2 \text{ eV}$ for Rh and Ir for $\text{Ca}_3\text{CoMO}_6 \ (M = \text{Rh, Ir})$. (We note that LSDA+$U$ and LSDA+$U$+SOC calculations, only the difference $U - J = U_{\text{eff}}$ matters for the calculations.) These parameters are quite similar to those employed by Wu et al. in their DFT studies of $\text{Ca}_3\text{Co}_2\text{O}_6$ and $\text{Ca}_3\text{CoRhO}_6$. We also employed these parameters for our LSDA+$U$+SOC (WIEN2k) calculations on $\text{Ca}_3\text{CoMO}_6 \ (M = \text{Co, Rh, Ir})$ to find that the use of $U_{\text{eff}} = 4$ and $2 \text{ eV}$ on Co and M, respectively, does not lead to magnetic insulating states for $\text{Ca}_3\text{CoMO}_6 \ (M = \text{Rh, Ir})$, but the use of $U_{\text{eff}} = 4 \text{ eV}$ on both Co and M does. Hereafter, the $U_{\text{eff}}$ values on Co, Rh and Ir will be designated as $U_{\text{eff}}(\text{Co})$, $U_{\text{eff}}(\text{Rh})$ and $U_{\text{eff}}(\text{Ir})$, respectively.

Possible ordered spin arrangements for each CoMO$_6$ chain of $\text{Ca}_3\text{CoMO}_6 \ (M = \text{Co, Rh, Ir})$ include the FM (i.e., ↑↑↑↑), antiferromagnetic (AFM) (i.e., ↑↓↑↓) and ↑↑↓↓ arrangements. It should be noted that the AFM state represents a ferrimagnetic arrangement in each CoMO$_6$ chain because the magnetic moments of the Co and M sites are different (see below). In our calculations, the spin arrangement between adjacent CoMO$_6$ chains is assumed to be FM.
3. Magnetic ground states of Ca₃CoM₆ (M = Co, Rh, Ir)

Our WIEN2k calculations show that, for Ca₃Co₂O₆, a magnetic insulating state can be obtained at the LSDA+U and LSDA+U+SOC levels of calculations, but the LSDA+U+SOC level of calculations are necessary to obtain the L = 2 configuration \((d_0)^1(d_2, d_2)^3(d_1, d_1)^2\) for the TP Co³⁺ ion, as found by Wu et al. For both Ca₃CoRhO₆ and Ca₃CoIrO₆, a magnetic insulating state is obtained only at the LSDA+U+SOC level of calculations. Our LSDA+U+SOC calculations reveal that only the FM state is stable for the experimental structure of Ca₃Co₂O₆, while both the FM and ↑↑↓↓ states are stable for the experimental structure of Ca₃CoRhO₆. The FM state is more stable than the ↑↑↓↓ state by 308 meV per formula unit (FU) from calculations with \(U_{\text{eff}}(\text{Co}) = 4\ \text{eV}\) and \(U_{\text{eff}}(\text{Rh}) = 2\ \text{eV}\), and by 422 meV/FU from calculations with \(U_{\text{eff}}(\text{Co}) = U_{\text{eff}}(\text{Rh}) = 4\ \text{eV}\). For the optimized structure of Ca₃CoIrO₆ with C₃ symmetry, only the AFM state is stable as long as \(U_{\text{eff}}(\text{Co}) \geq U_{\text{eff}}(\text{Ir})\) in LSDA+U+SOC calculations. When \(U_{\text{eff}}(\text{Co}) < U_{\text{eff}}(\text{Ir})\), LSDA+U+SOC calculations lead to a stable FM state, but the FM state is less stable than the AFM state (e.g., by 39 meV/FU with \(U_{\text{eff}}(\text{Co}) = 3.5\ \text{eV}\) and \(U_{\text{eff}}(\text{Ir}) = 4.0\ \text{eV}\)).

4. Jahn-Teller distortion and magnetic anisotropy

To see whether Ca₃CoMO₆ (M = Co, Rh, and Ir) undergoes a JT distortion, all the structures of Ca₃CoMO₆ (M = Co, Rh, and Ir) were optimized by performing LSDA+U+SOC (VASP) calculations with the //c-spin orientation for their FM states. In the geometry optimizations, the cell parameters were fixed at the experimental values, but the atom positions were allowed to relax with and without the C₃ rotational symmetry for each CoMO₆.
The atom positions of the optimized structures of Ca$_3$CoMO$_6$ (M = Co, Rh, Ir) are summarized in Tables S3.1 – S3.3 of the supporting information.

The relative energies of the experimental and optimized structures of Ca$_3$CoMO$_6$ (M = Co, Rh, Ir) obtained by LSDA+U+SOC (VASP) calculations are summarized in Table 3.1, and the spin and orbital moments (µ$_S$ and µ$_L$, respectively) of the TP and OCT transition-metal ions of Ca$_3$CoMO$_6$ (M = Co, Rh, Ir) obtained by the LSDA+U+SOC (WIEN2k) calculations in Tables 3.2 – 3.4. For the optimized structure with C$_3$ rotational symmetry, the orbital moment on the TP Co$^{n+}$ ion is large (i.e., µ$_L$ = 1.48, 1.68 and 1.69 µ$_B$ for M = Co, Rh and Ir, respectively). However, for the optimized structure without C$_3$ symmetry, the orbital moment on the TP Co$^{n+}$ ion is smaller (i.e., µ$_L$ = 0.47, 0.60 and 0.30 µ$_B$ for M = Co, Rh and Ir, respectively). (The spin and orbital moments of the OCT sites will be discussed in Section 6.) For each Ca$_3$CoMO$_6$ (M = Co, Rh or Ir), the optimized structure without C$_3$ symmetry is more stable than that with C$_3$ symmetry (i.e., ΔE = 65.5, 35.2 and 139.8 meV per FU for M = Co, Rh and Ir, respectively). This shows that the structural change of Ca$_3$CoMO$_6$ (M = Co, Rh or Ir), from the structure with C$_3$ symmetry to that without C$_3$ symmetry, is a JT distortion. Fig. 3.4 shows the atom displacements involved in the JT distortions of Ca$_3$CoMO$_6$ (M = Co, Rh, Ir), with respect to the experimental structure for M = Co and Rh, and with respect to the optimized structure with C$_3$-rotational symmetry for M = Ir. In Ca$_3$Co$_2$O$_6$ with TP Co$^{3+}$ ions, the largest displacement (0.064 Å) is found for one of the O atoms with a smaller displacement for the TP Co atom (i.e., 0.027 Å). In Ca$_3$CoRhO$_6$ and Ca$_3$CoIrO$_6$ with TP Co$^{2+}$ ions, however, the TP Co atom shows the largest displacement (i.e.,
0.064 and 0.051 Å, respectively). A probable cause for this difference is discussed in Section 7.

An important consequence of the JT distortion is that the orbital moments of the TP Co\(^{n+}\) ions are reduced by the JT distortion but the JT distortions are not strong enough to completely quench the orbital angular moment of Co\(^{n+}\) (Tables 3.2 – 3.4). As found for Ca\(_3\)CoMnO\(_6\),\(^4\) therefore, the oxides Ca\(_3\)CoMO\(_6\) (M = Co, Rh, Ir) cannot possess a genuine uniaxial magnetism. We investigate the preference of their spin orientation by performing LSDA+U+SOC (WIEN2k) calculations for the JT-distorted Ca\(_3\)Co\(_2\)O\(_6\), Ca\(_3\)CoRhO\(_6\) and Ca\(_3\)CoIrO\(_6\) with //c- and ⊥c-spin orientations. Our calculations show that the ⊥c-spin orientation is less stable than the //c-spin orientation by 33, 26 and 27 meV/FU for Ca\(_3\)Co\(_2\)O\(_6\), Ca\(_3\)CoRhO\(_6\) and Ca\(_3\)CoIrO\(_6\), respectively, which represent very strong easy-axis anisotropy. This renders the observed anisotropic magnetic character to Ca\(_3\)Co\(_2\)O\(_6\), Ca\(_3\)CoRhO\(_6\) and Ca\(_3\)CoIrO\(_6\).

5. One-electron picture in DFT+U description: Analysis of the electronic structure of Ca\(_3\)Co\(_2\)O\(_6\)

In general, it is not straightforward to decipher a one-electron picture hidden behind the results of DFT calculations especially when the latter include effects of spin-polarization/on-site repulsion.\(^{36}\) To estimate the energy separation \(\Delta_1\) between \(d_0\) and \((d_2, d_{-2})\) as well as the energy separation \(\Delta_2\) between \((d_2, d_{-2})\) and \((d_1, d_{-1})\) (see Fig. 3.2a) of the TP Co\(^{3+}\) ion in Ca\(_3\)Co\(_2\)O\(_6\), one may perform one-electron tight binding-calculations for an isolated TP CoO\(_6\). The CoO\(_6\) TP found in Ca\(_3\)Co\(_2\)O\(_6\) differs slightly from the ideal CoO\(_6\) TP
in that the two \( \text{O}_3 \) triangular faces are not eclipsed but are rotated away from each other around the \( C_3 \) axis by the angle \( \phi = 14.25^\circ \). Our extended Hückel tight-binding calculations\textsuperscript{37,38} for the \( \text{CoO}_6 \) TP show that \( \Delta_1 = 0.20 \text{ eV} \) and \( \Delta_2 = 0.65 \text{ eV} \) for the \( \text{CoO}_6 \) TP with \( \phi = 0^\circ \), while \( \Delta_1 = 0.13 \text{ eV} \) and \( \Delta_2 = 0.74 \text{ eV} \) for the \( \text{CoO}_6 \) TP with \( \phi = 14.25^\circ \). (The atomic parameters used for these calculations are summarized in Table S3.4 of the supporting information.) Thus, \( \Delta_1 (0.13 – 0.20 \text{ eV}) \) is greater than the typical SOC energy expected for 3d transition metal oxides (i.e., less than 0.05 eV)\textsuperscript{39} by a factor of 3 – 4, and is smaller than \( \Delta_2 \) only by a factor of 3 – 6. Consequently, the correct d-state split pattern for the TP \( \text{Co}^{3+} \) ions of \( \text{Ca}_3\text{CoMO}_6 \) should be \( d_0 < (d_2, d_{-2}) < (d_1, d_{-1}) \) with \( \Delta_1 = 0.13 – 0.20 \text{ eV} \) and \( \Delta_2 = 0.65 – 0.74 \text{ eV} \). In the following we examine how this split pattern is manifested in the LSDA+U and LSDA+U+SOC calculations for \( \text{Ca}_3\text{Co}_2\text{O}_6 \).

As reported by Wu \textit{et al.},\textsuperscript{21} our study for \( \text{Ca}_3\text{Co}_2\text{O}_6 \) shows that the TP \( \text{Co}^{3+} \) ion has the \( L = 2 \) configuration \((d_0)^1(d_2, d_{-2})^3(d_1, d_{-1})^2\) in the LSDA+U+SOC calculations but the \( L = 0 \) configuration \((d_0)^2(d_2, d_{-2})^2(d_1, d_{-1})^2\) in the LSDA+U calculations. This can be seen from the projected DOS plots presented in Fig. 3.5. To understand the switching of the \( L = 0 \) configuration to the \( L = 2 \) configuration by the action of SOC, it is necessary to consider three effects, i.e., the spin arrangement between adjacent TP and OCT \( \text{Co}^{3+} \) ions,\textsuperscript{1,40} the direct metal-metal interaction between them, and the SOC on the TP \( \text{Co}^{3+} \) ion.\textsuperscript{21,40} It is convenient to discuss these factors by considering an isolated dimer made up of adjacent TP \( \text{CoO}_6 \) and OCT \( \text{CoO}_6 \), as pointed out elsewhere.\textsuperscript{40}
We first consider the interaction between the $z^2$ orbitals of adjacent Co$^{3+}$ ions. In a one-electron tight-binding description, the high-spin Co$^{3+}$ ($d^6$) ion of an isolated TP CoO$_6$ has the $(d_0)^2(d_2, d_{-2})^2(d_1, d_{-1})^2$ configuration while the low-spin Co$^{3+}$ ($d^6$) ion of an isolated OCT CoO$_6$ has the $(t_{2g})^6$ configuration. The OCT CoO$_6$ in Ca$_3$Co$_2$O$_6$ has $C_3$ symmetry, so the $t_{2g}$ level is split into the 1a and 1e set as depicted in Fig. 3.2b. The $z^2$ orbital of the TP Co$^{3+}$ ion can interact directly with the 1a orbital (i.e., the $z^2$ orbital) of the OCT Co$^{3+}$ ion through the shared triangular face due to the very short NN Co…Co distance (2.595 Å). In describing such an interaction at the spin-polarized DFT+U level, it should be noted that one-electron energy levels given by tight-binding calculations are split into the up-spin and down-spin levels by the spin-polarization/on-site repulsion, as illustrated in Fig. 3.6. Thus, the $L = 0$ configuration $(d_0)^2(d_2, d_{-2})^2(d_1, d_{-1})^2$ of the TP Co$^{3+}$ ion means that the LUMO of the TP CoO$_6$ is given by the $(d_2, d_{-2})\downarrow$ level. Therefore, if one of the four electrons present in the two $z^2$ orbitals of adjacent TP and OCT Co$^{3+}$ ions is transferred to the $(d_2, d_{-2})\downarrow$ level of the TP Co$^{3+}$ ion, the resulting electron configuration of the TP Co$^{3+}$ ion would be close to $(d_0)^1(d_2, d_{-2})^3(d_1, d_{-1})^2$. The spins of the TP and OCT Co$^{3+}$ ions are assumed to have the FM arrangement in Fig. 3.7a, where the $z^2\uparrow$ and $z^2\downarrow$ levels of the OCT Co$^{3+}$ ion are split less than those of the TP Co$^{3+}$ ion because, to a first approximation, the OCT site has a low-spin Co$^{3+}$ ion whereas the TP site has a high-spin Co$^{3+}$ ion. Since both TP and OCT sites have Co$^{3+}$ ions, the midpoint between their $z^2\uparrow$ and $z^2\downarrow$ levels should be nearly the same. The highest occupied level resulting from the $z^2$ orbitals of the two Co$^{3+}$ ions is the $\sigma^*\downarrow$ level, in which the weight of the TP $z^2\downarrow$ orbital is larger than the OCT $z^2\downarrow$ orbital because the former lies higher in
energy than the latter. In the DFT+U level of description, the occupied $\sigma^*\downarrow$ level lies below the empty $(d_2, d_2)\downarrow$ level of the TP Co$^{3+}$ ion. The effect of the SOC interaction at the TP Co$^{3+}$ ion site is depicted in Fig. 3.8a, where the SOC splits the unoccupied degenerate level $(d_2, d_2)\downarrow$ into the $d_2\downarrow$-below-$d_2\downarrow$ pattern since $\lambda < 0$ for Co$^{3+}$ (d$^6$). When the unoccupied $d_2\downarrow$ level is lowered below the occupied $\sigma^*\downarrow$ level, an electron transfer occurs from the $\sigma^*\downarrow$ level to the $d_2\downarrow$ level. Since the $\sigma^*\downarrow$ level has a greater weight on the TP $z^2\downarrow$ orbital, this charge transfer effectively amounts to the configuration switch of the TP Co$^{3+}$ from the $L = 0$ configuration $(d_0)^2(d_2, d_2)^2(d_1, d_1)^2$ to the $L = 2$ configuration $(d_0)^1(d_2, d_2)^3(d_1, d_1)^2$. This is why the TP Co$^{3+}$ ion has the $(d_0)^2(d_2, d_2)^2(d_1, d_1)^2$ configuration at the DFT+U level, but has the $(d_0)^1(d_2, d_2)^3(d_1, d_1)^2$ configuration at the DFT+U+SOC level. This explanation is based on the d-state split pattern of $d_0 < (d_2, d_2) < (d_1, d_1)$ for the TP Co$^{3+}$ ion. If the TP Co$^{3+}$ ion were to have the $(d_2, d_2) < d_0 < (d_1, d_1)$ split pattern (Fig. 3.8b), the TP Co$^{3+}$ ion would have the $(d_0)^1(d_2, d_2)^3(d_1, d_1)^2$ configuration in both DFT+U and DFT+U+SOC levels of descriptions because the $\sigma^*\downarrow$ level remains unoccupied regardless of whether or not the singly occupied $(d_2, d_2)\downarrow$ level is split by the effect of SOC.

6. Electronic structures of Ca$_3$CoMO$_6$ (M = Rh, Ir)

The reason why Ca$_3$CoMO$_6$ (M = Rh, Ir) has Co$^{2+}$ and M$^{4+}$ ions in the TP and OCT sites is that the Co 3d orbital lies lower in energy, and is more contracted, than the Rh 4d and Ir 5d orbitals. Thus, the essential features of the direct metal-metal interaction between the TP Co$^{2+}$ and OCT Rh$^{4+}$ ions, which give rise to the configuration $(z^2)^2(x^2-y^2, xy)^3(xz, yz)^2$ for
the TP Co\(^{2+}\) ion and the configuration \((1a)^1(1e)^4\) for the OCT Rh\(^{4+}\) ion, can be understood in terms of the orbital interaction diagram shown in Fig. 3.9a. Here the two adjacent ions have the FM arrangement, and the midpoint between the \(z^2\uparrow\) and \(z^2\downarrow\) orbitals is placed higher in energy for the M\(^{4+}\) (M = Rh, Ir) ion than that for the Co\(^{2+}\) ion, because the Rh 4d and Ir 5d orbital is more diffuse, and lies higher in energy, than the Co 3d orbital.\(^{38,41}\) The \(\sigma^*\downarrow\) level (i.e., the highest-lying level arising from the interactions between the \(z^2\) orbitals of adjacent Co\(^{2+}\) and M\(^{4+}\) site) has a larger weight on the OCT M\(^{4+}\) ion so that the absence of an electron in the \(\sigma^*\downarrow\) level amounts to the \(\text{(1a)}^1(\text{1e})^4\) configuration for the OCT M\(^{4+}\) ion.

The low-spin OCT M\(^{4+}\) (d\(^5\)) ion of Ca\(_3\)CoM\(_6\) (M = Rh, Ir) has the open-shell configuration, \((t_{2g})^5\), and the Rh and Ir atoms are a heavier element than Co. Therefore, the local electronic structure of M\(^{4+}\) (d\(^5\)) ion can be more strongly affected by the SOC compared with that of the OCT Co\(^{3+}\) (d\(^6\)) ion in Ca\(_3\)Co\(_2\)O\(_6\). In principle, the \((t_{2g})^5\) configuration can be approximated by either \((1a)^1(1e)^4\) or \((1a)^2(1e)^3\) (see Fig. 3.2b). The angular momentum behavior of the 1a (i.e., \(z^2\)) orbital is described by \(d_0\), and those of the 1e orbitals by linear combinations of \(d_{\pm1}\) and \(d_{\pm2}\), namely, by \(\sqrt{2/3}(x^2 - y^2) - \sqrt{1/3}yz\) and \(\sqrt{2/3}xy - \sqrt{1/3}xz\).\(^{42}\) Thus, the orbital moment \(\mu_L\) of the OCT M\(^{4+}\) (d\(^5\)) ion would be negligible if its electron configuration is close to \((1a)^1(1e)^4\). However, this would not be the case if the electron configuration is close to \((1a)^2(1e)^3\). As discussed below, it depends on the spin arrangement between adjacent Co\(^{2+}\) and M\(^{4+}\) ions, the direct metal-metal interaction between them, and the SOC of the M\(^{4+}\) ion whether the local electronic structure of the OCT M\(^{4+}\) (d\(^5\)) ion is close to \((1a)^1(1e)^4\) or to \((1a)^2(1e)^3\).
As shown by the projected DOS plots for the FM state of Ca$_3$CoRhO$_6$ in Fig. 3.10, the LSDA+U+SOC (WIEN2k) calculations with $U_{\text{eff}}(\text{Co}) = U_{\text{eff}}(\text{Rh}) = 4$ eV predict Ca$_3$CoRhO$_6$ to be a magnetic insulator, whereas our LSDA+U calculations with $U_{\text{eff}}(\text{Co}) = U_{\text{eff}}(\text{Rh}) = 4$ eV predict Ca$_3$CoRhO$_6$ to be a metal (See Fig. S3.1 of the supporting information). (The LSDA+ U and LSDA+U+SOC calculations with $U_{\text{eff}}(\text{Co}) = 4$ eV and $U_{\text{eff}}(\text{Rh}) = 2$ eV both predict Ca$_3$CoRhO$_6$ to be a metal. See Fig. S3.2a and S3.2b of the supporting information). The projected DOS plots from the LSDA+U+SOC calculations show that the local electronic structure of the TP Co$^{2+}$ ion is given by $(z^2)^2(x^2-y^2, \text{xy})^3(xz, yz)^2$, and that of the OCT Rh$^{4+}$ ion by $(1a)^1(1e)^4$. This explains the uniaxial magnetism of Ca$_3$CoRhO$_6$ brought about by the $L = 2$ configuration of the TP Co$^{2+}$ ion, and why the orbital moment $\mu_L$ of the OCT Rh$^{4+}$ ion is nearly zero (see Table 3.3) in the LSDA+U+SOC calculations.

The above discussion for the FM state of Ca$_3$CoRhO$_6$, which accounts for the configuration $(z^2)^2(x^2-y^2, \text{xy})^3(xz, yz)^2$ for the TP Co$^{2+}$ ion and the configuration $(1a)^1(1e)^4$ for the OCT Rh$^{4+}$ ion, is also applicable to the FM state of Ca$_3$CoIrO$_6$. The AFM spin arrangement (i.e., the ferrimagnetic state) of Ca$_3$CoIrO$_6$ has a slightly different picture for the local electronic structure of the OCT Ir$^{4+}$ ion. The projected DOS plots for the AFM state are presented in Fig. 3.11, where the OCT Ir$^{4+}$ ion is not described by $(1a)^1(1e)^4$ but by $(1a)^2(1e)^3$. (The LSDA+ U and LSDA+U+SOC calculations with $U_{\text{eff}}(\text{Co}) = 4$ eV and $U_{\text{eff}}(\text{Ir}) = 2$ eV both predict Ca$_3$CoIrO$_6$ to be a metal. See Fig. S3.3 of the supporting information.) As a consequence, the orbital moment $\mu_L$ of the OCT Ir$^{4+}$ ion is large (Table 3.4). This observation is explained by noting from Fig. 3.9 that the $\sigma^*\downarrow$ level of the dimer made up of
adjacent TP Co$^{2+}$ and OCT Ir$^{4+}$ ions would lie lower in energy in the AFM than in the FM spin arrangement, because the energy gap between the $z^2\downarrow$ orbitals of the two ions is greater for the AFM arrangement. The $1\text{e}\downarrow$ level of the OCT Ir$^{4+}$ ion is split by SOC, and the OCT Ir$^{4+}$ ion adopts the $(1a)^2(1e)^3$ configuration when the upper one of the split $1\text{e}\downarrow$ level becomes higher in energy than the $\sigma^*\downarrow$ level (Fig. 3.12). Since the Ir$^{4+}$ ion has a stronger SOC than does the Rh$^{4+}$ ion, the split of the $1\text{e}\downarrow$ level is larger in Ca$_3$CoIrO$_6$ than in Ca$_3$CoRhO$_6$. In addition, the Co…Ir metal-metal interaction is weaker than the Co…Rh metal-metal interaction because the NN Co…Ir distance is longer than the NN Co…Rh distance. This makes the $1\text{e}\downarrow$ level lying lower in Ca$_3$CoIrO$_6$ than in Ca$_3$CoRhO$_6$. Consequently, the OCT Rh$^{4+}$ ion has the $(1a)^1(1e)^4$ configuration, but the OCT Ir$^{4+}$ ion the $(1a)^2(1e)^3$ configuration.

7. Discussion

For the SOC effect to induce electron transfer from the $\sigma^*\downarrow$ level to the $d_2\downarrow$ level in Ca$_3$Co$_2$O$_6$ (Fig. 3.7a), the $\sigma^*\downarrow$ level should lie high in energy because the split between the $d_2$ and $d_2$ levels by SOC is not large for a 3d transition metal ion. Important factors raising the $\sigma^*\downarrow$ level are the direct metal-metal interaction and the FM spin arrangement between adjacent Co$^{3+}$ ions. Compared with the AFM arrangement (Fig. 3.7b), the FM arrangement has a smaller energy difference between the $z^2\downarrow$ orbitals of the TP and OCT Co$^{3+}$ ions, which leads to a stronger interaction between them hence raising the $\sigma^*\downarrow$ level higher. Another important factor is that the TP and OCT sites both have Co$^{3+}$ ions with similarly contracted $z^2\downarrow$ orbitals so that the overlap between them is good hence raising the $\sigma^*\downarrow$ level.
In the LSDA+U+SOC calculations, both the $\sigma^{\uparrow}$ and $\sigma^*\uparrow$ levels are both occupied. In contrast, the $\sigma^{\downarrow}$ level is filled but the $\sigma^*\downarrow$ level is not. Consequently, the Co…Co metal-metal interaction in Ca$_3$Co$_2$O$_6$ is overall bonding. This accounts for why the displacement of the TP Co$^{3+}$ ion is not large in the JT distorted structure of Ca$_3$Co$_2$O$_6$. This reasoning suggests that the Co…M metal-metal interaction in Ca$_3$CoMO$_6$ (M = Rh, Ir) should be weak because the TP Co$^{2+}$ ion has a large displacement in the JT distorted structure. The NN Co…Rh and Co…Ir distances of Ca$_3$CoRhO$_6$ and Ca$_3$CoIrO$_6$, respectively, are short (i.e., 2.682 and 2.706 Å, respectively) but are longer than the NN Co…Co distance (2.595 Å) of Ca$_3$Co$_2$O$_6$. Furthermore, the Co 3d and Rh 4d orbitals are different in orbital contractedness, and even more so are the Co 3d and Ir 5d orbitals. Consequently, the direct metal-metal interaction between Co$^{2+}$ and M$^{4+}$ ions in Ca$_3$CoMO$_6$ (M = Rh, Ir) would be weaker than that between Co$^{3+}$ ions in Ca$_3$Co$_2$O$_6$. This accounts for why the displacement of the TP Co$^{2+}$ ion is large in the JT distorted structures of Ca$_3$CoMO$_6$ (M = Rh, Ir).

The differences in the $z^2$ orbital occupations of the TP and OCT ions in Ca$_3$CoMO$_6$ (M = Co, Rh, Ir) are important to note. From the viewpoint of two adjacent TP and OCT ions, the highest-lying level resulting from their two $z^2$ orbitals is the $\sigma^*\downarrow$ level, which decreases in energy with lengthening the NN Co…M distance and with increasing the difference in the contractedness of the Co and M $z^2$ orbitals. Thus, it is understandable that the two $z^2$ orbitals of adjacent TP and OCT ions have four electrons in Ca$_3$CoIrO$_6$ (i.e., the $\sigma^*\downarrow$ level is occupied), but three electrons in Ca$_3$Co$_2$O$_6$ and Ca$_3$CoRhO$_6$ (i.e., the $\sigma^*\downarrow$ level is unoccupied). The latter is equivalent to a singly occupied $z^2$ orbital at the TP Co$^{3+}$ ion in Ca$_3$Co$_2$O$_6$, but that at the OCT Rh$^{4+}$ ion in Ca$_3$CoRhO$_6$, due to the unequal weights of the TP
and OCT $z^2$ orbitals in the $\sigma^*\downarrow$ level (Fig. 3.7 vs. Fig. 3.9). A higher-lying $\sigma^*\downarrow$ level and a lower-lying $\sigma\downarrow$ level are obtained when adjacent TP and OCT ions have an FM spin arrangement than an AFM spin arrangement. Thus, the FM arrangement is energetically more favorable when the $\sigma^*\downarrow$ level is unoccupied as found for Ca$_3$Co$_2$O$_6$ and Ca$_3$CoRhO$_6$, but an AFM arrangement is energetically more favorable when the $\sigma^*\downarrow$ level is occupied as found for Ca$_3$CoIrO$_6$.

8. Concluding remarks

In summary, the JT instability, uniaxial magnetism, spin arrangement, metal-metal interaction and spin-orbit coupling are intimately interrelated in Ca$_3$CoMO$_6$ (M = Co, Rh, Ir). The adjacent spins in each CoMO$_6$ chain of Ca$_3$CoMO$_6$ (M = Co, Rh, Ir) prefer the FM arrangement for M = Co and Rh, but the AFM arrangement for M = Ir. The magnetism of Ca$_3$CoMO$_6$ (M = Co, Rh, Ir) cannot be genuinely uniaxial because it undergoes a weak JT distortion. Nevertheless, the orbital moments of the TP Co$^{n+}$ ions, though strongly reduced by the distortion, are still substantial enough to produce strong easy-axis anisotropy along the chain direction. The d-state split pattern of the TP Co$^{n+}$ (n = 2, 3) ions that is consistent with the electronic and magnetic properties of Ca$_3$CoMO$_6$ (M = Co, Rh, Ir) is not $(d_2, d_2) < d_0 < (d_1, d_1)$, but $d_0 < (d_2, d_2) < (d_1, d_1)$. The $L = 2$ configuration $(d_0)^1(d_2, d_2)^2(d_1, d_1)^2$ of the TP Co$^{3+}$ ion in Ca$_3$Co$_2$O$_6$ is a combined consequence of the FM spin arrangement between adjacent TP and OCT Co$^{3+}$ ions, the direct metal-metal interaction between them mediated by their $z^2$ orbials, and the SOC of the TP Co$^{3+}$ ion. In contrast to the case of Ca$_3$Co$_2$O$_6$, the TP and OCT ions of Ca$_3$CoMO$_6$ (M = Rh, Ir) have different oxidation states (+2 and +4,
respectively), because the Co 3d orbital lies lower in energy, and is more contracted, than the Rh 4d and Ir 5d orbitals. The OCT M\(^{4+}\) ion has the \((1a)^1(1e)^4\) configuration for \(M = \text{Rh}\) but the \((1a)^2(1e)^3\) configuration for \(M = \text{Ir}\). This difference reflects a combined consequence of the spin arrangement between adjacent TP Co\(^{2+}\) and OCT M\(^{4+}\) ions, the direct metal-metal interaction between them mediated by their \(z^2\) orbitals, and the SOC of the TP M\(^{4+}\) ions.

Acknowledgments

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Supporting Information Available

Additional tables and figures. This material is available free of charge via the Internet at [http://pubs.acs.org](http://pubs.acs.org).
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(38) Our calculations were carried out by employing the SAMOA (Structure and Molecular Orbital Analyzer) program package (This program can be downloaded free of charge from the website, http://chvamw.chem.ncsu.edu/).


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Table 3.1. Relative energies $\Delta E$ (meV/FU) of the experimental and optimized structures of Ca$_3$CoMO$_6$ ($M$ = Co, Rh, Ir) obtained from the LSDA+U+SOC calculations using the PAW method of the VASP with $U_{\text{eff}} = 4$ eV for Co and $U_{\text{eff}} = 2$ eV for $M$ = Rh and Ir.$^a$

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$^a$ For each Ca$_3$CoMO$_6$ ($M$ = Co, Rh, Ir), the optimization was carried out for the FM state.
Table 3.2. Spin and orbital moments ($\mu_S$ and $\mu_L$, respectively) of the TP and OCT Co$^{3+}$ ions in the FM state of Ca$_3$Co$_2$O$_6$ obtained from the LSDA+U+SOC (WIEN2k)$^a$ calculations with $U_{\text{eff}}(\text{Co}) = 4$ eV.$^b,c$

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$^a$ Our LSDA+U+SOC (WIEN2k) optimization converges to the structure with no C$_3$-rotational symmetry. The numbers listed are obtained from our LSDA+U+SOC (VASP) optimization.

$^b$ The orbital and spin moments have the same direction when they have the same sign, and the opposite directions otherwise.

$^c$ There are two slightly different TP Co atoms as well as two slightly different OCT Co atoms in the optimized structures with or without C$_3$ symmetry.
Table 3.3. Spin and orbital moments ($\mu_S$ and $\mu_L$, respectively) of the TP Co$^{2+}$ and OCT Rh$^{4+}$ ions in the FM state of Ca$_3$CoRhO$_6$ obtained from the LSDA+U+SOC (WIEN2k) calculations with $U_{\text{eff}} (\text{Co}) = U_{\text{eff}} (\text{Rh}) = 4$ eV.$^{a,b}$

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$^a$ The orbital and spin moments have the same direction when they have the same sign, and the opposite directions otherwise.

$^b$ There are two slightly different TP Co atoms as well as two slightly different OCT Co atoms in the optimized structures with or without $C_3$ symmetry.
Table 3.4. Spin and orbital moments ($\mu_S$ and $\mu_L$, respectively) of the TP Co$^{2+}$ and OCT Ir$^{4+}$ ions in the AFM state of Ca$_3$CoIrO$_6$ obtained from the LSDA+U+SOC (WIEN2k) calculations with $U_{\text{eff}}$(Co) = $U_{\text{eff}}$(Ir) = 4 eV.$^{a,b}$

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$^a$ The orbital and spin moments have the same direction when they have the same sign, and the opposite directions otherwise.

$^b$ There are two slightly different TP Co atoms as well as two slightly different OCT Co atoms in the optimized structures with or without C$_3$ symmetry.
Figure 3.1. (a) Projection view of the crystal structure of Ca₃CoMO₆ along the c-direction. (b) Perspective view of an isolated CoMO₆ chain. The grey, purple, blue and red balls represent Ca, Co, M, and O atoms, respectively.
Figure 3.2. Shapes and relative energies of (a) the d-states of the CoO$_6$ trigonal prism and (b) the t$_{2g}$-states of the CoO$_6$ octahedron of Ca$_3$Co$_2$O$_6$ obtained from extended Hückel tight-binding calculations.
Figure 3.3. High-spin electron configurations expected for the Co\textsuperscript{3+} (d\textsuperscript{6}) and Co\textsuperscript{2+} (d\textsuperscript{7}) ions at a trigonal prism site when the d-state split pattern is given by d\textsubscript{0} < (d\textsubscript{2}, d\textsubscript{-2}) < (d\textsubscript{1}, d\textsubscript{-1}) in (a), (b) and (e), and by (d\textsubscript{2}, d\textsubscript{-2}) < d\textsubscript{0} < (d\textsubscript{1}, d\textsubscript{-1}) in (c) and (d).
Figure 3.4. Displacements of the atoms associated with the Jahn-Teller distortions in the magnetic ground state of (a) Ca$_3$Co$_2$O$_6$, (b) Ca$_3$CoRhO$_6$, and (c) Ca$_3$CoIrO$_6$ with respect to their positions of the experimental structures for Ca$_3$Co$_2$O$_6$ and Ca$_3$CoRhO$_6$, and with respect to their positions of the optimized structure with $C_3$ symmetry for Ca$_3$CoIrO$_6$. The largest atom displacement is 0.044 Å in Ca$_3$Co$_2$O$_6$, 0.064 Å in Ca$_3$CoRhO$_6$, and 0.051 Å in Ca$_3$CoIrO$_6$. In each figure, the left side shows a perspective view of the atom displacements in the CoMO$_6$ chain, and the right side the projection view (along the chain direction) of the atom displacements in the CoO$_6$ trigonal prisms and MO$_6$ octahedra.
Figure 3.5. Projected DOS plots for the $z^2$, $(x^2-y^2 + xy)$ and $(xz + yz)$ states of the TP and OCT Co$^{3+}$ ions in the FM state of Ca$_3$Co$_2$O$_6$ obtained from the LSDA+U and LSDA+U+SOC calculations by using the FPLAPW method of the WIEN2k package, the experimental structure of Ca$_3$Co$_2$O$_6$, and $U_{\text{eff}}$(Co) = 4 eV.
Figure 3.6. Schematic representations of the high-spin electron configuration of the trigonal prism Co$^{3+}$ (d$^6$) in (a) the one-electron picture and (b) the spin-polarized DFT+U level of description.
Figure 3.7. DFT+U level description of the orbital interactions between the $z^2$ orbitals of adjacent TP and OCT Co$^{3+}$ ions in Ca$_3$Co$_2$O$_6$ that lead to the $\sigma$ and $\sigma^*$ orbitals when the spins of the two Co$^{3+}$ sites have a (a) ferromagnetic and (b) an antiferromagnetic arrangement.

Figure 3.8. Effect of the SOC at the TP Co$^{3+}$ ion on the occupancy of the $\sigma^*\downarrow$ level of a dimer unit consisting of two adjacent TP and OCT Co$^{3+}$ ions in Ca$_3$Co$_2$O$_6$ for cases when the d-state split pattern of the TP Co$^{3+}$ ion is given by (a) $d_0 < (d_2, d_{-2}) < (d_1, d_{-1})$ and (b) $(d_2, d_{-2}) < d_0 < (d_1, d_{-1})$. 
Figure 3.9. Orbital interactions between the $z^2\downarrow$ orbitals of adjacent TP Co$^{2+}$ and OCT M$^{4+}$ ions in Ca$_3$CoMO$_6$ ($M = $ Rh, Ir) that lead to the $\sigma\downarrow$ and $\sigma^*\downarrow$ orbitals when the spins of the two ion sites have (a) an FM and (b) an AFM arrangement. The midpoint between the $z^2\uparrow$ and $z^2\downarrow$ orbitals is higher in energy for the M$^{4+}$ (M = Rh, Ir) ion than that for the Co$^{2+}$ ion, because the Rh 4d and Ir 5d orbital is more diffuse, and lies higher in energy, than the Co 3d orbital. The $\sigma^*\downarrow$ orbital lies higher in energy in the FM than in the AFM spin arrangement.
Figure 3.10. Projected DOS plots for the $z^2$, $(x^2-y^2+xy)$ and $(xz+yz)$ states of the TP Co$^{2+}$ and OCT Rh$^{4+}$ ions in the FM state of Ca$_3$CoRhO$_6$ obtained from the LSDA+U+SOC calculations by using the FPLAPW method of the WIEN2k package, the experimental structure of Ca$_3$CoRhO$_6$, and $U_{\text{eff}} = 4$ eV on both Co and Rh.
Figure 3.11. Projected DOS plots for the $z^2$, $(x^2-y^2+xy)$ and $(xz+yz)$ states of the TP Co$^{2+}$ and OCT Ir$^{4+}$ ions in the AFM state of Ca$_3$CoIrO$_6$ obtained from the LSDA+U+SOC calculations by using the FPLAPW method of the WIEN2k package, the experimental structure of Ca$_3$CoIrO$_6$, and $U_{\text{eff}}(\text{Co}) = U_{\text{eff}}(\text{Ir}) = 4$ eV.
Figure 3.12. SOC effects on the 1e↓ level of the OCT M^{4+} ion and on the occupancy of the σ*↓ level of a dimer made up of two adjacent TP Co^{2+} and OCT M^{4+} ions in Ca_3CoMO_6 (M = Rh, Ir): (a) Ca_3CoRhO_6 and (b) Ca_3CoIrO_6.
Table S3.1. Fractional coordinates of the optimized structures of Ca₃Co₂O₆ from LDA+U+SOC (VASP) calculations (see the text)

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Table S3.2. Fractional coordinates of the optimized structures of Ca₃CoRhO₆ from LDA+U+SOC (VASP) calculations (see the text)

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Table S3.3. Fractional coordinates of the optimized structures of Ca$_3$CoIrO$_6$ from LDA+U+SOC (VASP) calculations (see the text)

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^a] H_{ii}'s are the diagonal matrix elements \( \langle \chi_i | H^{\text{eff}} | \chi_i \rangle \), where H^{\text{eff}} is the effective Hamiltonian.

In our calculations of the off-diagonal matrix elements H_{ij} = \( \langle \chi_i | H^{\text{eff}} | \chi_j \rangle \), the weighted formula was used. See: Ammeter, J.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R., *J. Am. Chem. Soc.* **1978**, *100*, 3686.
Figure S3.1. Projected DOS plots for the $z^2$, $(x^2-y^2 + xy)$ and $(xz + yz)$ states of the TP Co$^{2+}$ and OCT Rh$^{4+}$ ions in the FM state of Ca$_3$CoRhO$_6$ obtained from the LSDA+U calculations by using the FPLAPW method of the WIEN2k package, the experimental structure of Ca$_3$CoRhO$_6$, and $U_{\text{eff}}(\text{Co}) = U_{\text{eff}}(\text{Rh}) = 4$ eV.
Figure S3.2a. Projected DOS plots for the $z^2$, $(x^2-y^2 + xy)$ and $(xz + yz)$ states of the TP Co$^{2+}$ and OCT Rh$^{4+}$ ions in the FM state of Ca$_3$CoRhO$_6$ obtained from the LSDA+U calculations by using the FPLAPW method of the WIEN2k package, the experimental structure of Ca$_3$CoRhO$_6$, and $U_{\text{eff}}(\text{Co}) = 4$ eV and $U_{\text{eff}}(\text{Rh}) = 2$ eV.
Figure S3.2b. Projected DOS plots for the $z^2$, $(x^2-y^2+xy)$ and $(xz+yz)$ states of the TP Co$^{2+}$ and OCT Rh$^{4+}$ ions in the FM state of Ca$_3$CoRhO$_6$ obtained from the LSDA+U+SOC calculations by using the FPLAPW method of the WIEN2k package, the experimental structure of Ca$_3$CoRhO$_6$, and $U_{\text{eff}}$(Co) = 4 eV and $U_{\text{eff}}$(Rh) = 2 eV.
Figure S3.3. Projected DOS plots for the $z^2$, $(x^2-y^2 + xy)$ and $(xz + yz)$ states of the TP Co$^{2+}$ and OCT Ir$^{4+}$ ions in the FM state of Ca$_3$CoIrO$_6$ obtained from the LSDA+U and LSDA+U+SOC calculations by using the FPLAPW method of the WIEN2k package, the optimized structure of Ca$_3$CoIrO$_6$ with C$_3$ symmetry, and $U_{\text{eff}}$($\text{Co}$) = 4 eV and $U_{\text{eff}}$($\text{Ir}$) = 2 eV.
CHAPTER 4

Density functional investigation of the magnetic structure and ferroelectric polarization of the layered triangular antiferromagnet CuFeO₂ under magnetic field

A paper submitted to Chemistry of Materials

Yuemei Zhang¹, Erjun Kan² and Myung-Hwan Whangbo¹*

¹ Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204
² Department of Applied Physics, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, P. R. China

Abstract

The magnetic structure and ferroelectric polarization of the layered triangular antiferromagnet CuFeO₂ under magnetic field were probed on the basis of density functional calculations, and are compared with those of its isostructural multiferroic AgCrO₂. We probed why CuFeO₂ requires a magnetic field to adopt a helical spiral-spin structure but AgCrO₂ does not, by evaluating the relative stabilities of their helical spiral and collinear spin structures in terms of the calculated spin exchange parameters. In addition, we investigated how the ferroelectric polarization in CuFeO₂ is related to the asymmetric electron density distribution induced by helical spiral-spin order and to the handedness of the helical spin rotation.

mike_whangbo@ncsu.edu
1. Introduction

Multiferroic (i.e., magnetic ferroelectric) materials have received much attention due to the potential of controlling their physical properties by either magnetic or electric field.\textsuperscript{1-7} A centrosymmetric crystalline solid can become ferroelectric (FE) when it loses inversion symmetry, which is often induced either by cooperative Jahn-Teller distortion\textsuperscript{2,8} or by chiral magnetic order.\textsuperscript{6,9-14} The FE polarization driven by magnetic order has been discussed in terms of exchange striction\textsuperscript{15,16} or spin-orbit coupling (SOC).\textsuperscript{17-21} The FE polarization in one-dimensional magnetic systems with spiral-spin order is explained by the Katsura-Nagaosa-Balatsky model,\textsuperscript{21} which predicts that an isolated chain with cycloidal spiral-spin order gives rise to FE polarization along the direction perpendicular to the chain, but that with helical spiral-spin or sinusoidal-spin order has no FE polarization. The layered triangular antiferromagnets such as CuFeO\textsubscript{2} and AgCrO\textsubscript{2} exhibit FE polarization when their magnetic structure acquires a helical spiral-spin order in the chains of M\textsuperscript{3+} (M = Fe, Cr) ions of their MO\textsubscript{2} layers, and the direction of their FE polarization has been explained by considering the symmetry of the spin arrangements in the MO\textsubscript{2} layers.\textsuperscript{22,23}

The FeO\textsubscript{2} layers of CuFeO\textsubscript{2} are made up of edge-sharing FeO\textsubscript{6} octahedra\textsuperscript{24-26} containing high-spin Fe\textsuperscript{3+} (d\textsuperscript{5}, S = 5/2) ions (Fig. 4.1a).\textsuperscript{27,28} Each FeO\textsubscript{2} layer can be viewed in terms of the FeO\textsubscript{4} chains of edge-sharing FeO\textsubscript{6} octahedra running along the a-, b- or (a+b)-direction. Adjacent FeO\textsubscript{2} layers of CuFeO\textsubscript{2} are stacked along the c-direction with Cu\textsuperscript{+} (d\textsuperscript{10}) ions intercalated between the FeO\textsubscript{2} layers to form linear O-Cu-O bridges (Fig. 4.1b) such that there are three FeO\textsubscript{2} layers per unit cell. The magnetic ground state of CuFeO\textsubscript{2} has the ↑↑↓↓ spin arrangement in each FeO\textsubscript{2} layer (Fig. 4.2a) with their spins parallel to the c-axis.\textsuperscript{29} This
magnetic structure is modified by magnetic field \( H \) applied along the \( c \)-direction; the magnetic structure changes from the \( \uparrow \uparrow \downarrow \downarrow \) arrangement under \( H < \sim 7 \) T to the helical spiral-spin structure under \( H \approx 7 \sim 13 \) T to the \( \uparrow \uparrow \uparrow \downarrow \downarrow \) structure (Fig. 4.2b) under \( H > \sim 13 \) T.\(^{30}\) The helical spiral-spin state can also be induced into CuFeO\(_2\) without applying magnetic field by doping the Fe sites with Al or Ga atoms.\(^{31\text{-}35}\)

In the spiral-spin state of CuFeO\(_2\) below \( \sim 10 \) K, the spins of each FeO\(_2\) layer are separated into helical spiral-spin chains of Fe\(^{3+}\) ions leading to FE polarization (\(~200 \mu\)C/m\(^2\)).\(^{30,32,33}\) In the isostructural multiferroic AgCrO\(_2\), made up of edge-sharing CrO\(_6\) octahedra with Cr\(^{3+}\) (\(d^3, S = 3/2\)) ions, FE polarization (\(~5 \mu\)C/m\(^2\)) occurs below \( \sim 21 \) K without applied magnetic field, because AgCrO\(_2\) adopts a helical spiral-spin state in the absence of magnetic field.\(^{36,37}\) So far, it is not well understood why the magnetic structure of CuFeO\(_2\) changes from a collinear to a helical spiral to another collinear spin arrangement with increasing the strength of magnetic field applied parallel to the \( c \)-axis. It was controversial whether CuFeO\(_2\) is a Heisenberg or an Ising magnetic system.\(^{38,39}\) It has been suggested that the apparent Ising behavior of CuFeO\(_2\) results from an extrinsic factor such as oxygen vacancy.\(^{39}\) The spin exchange interactions and the FE polarization of AgCrO\(_2\) have already been examined by density functional calculations,\(^{23}\) but there has been no corresponding study for CuFeO\(_2\).

To explore why CuFeO\(_2\) requires a magnetic field applied parallel to the \( c \)-axis to have a helical spiral spin order whereas AgCrO\(_2\) does not, it is necessary to evaluate the spin exchange interactions of CuFeO\(_2\) on the basis of density functional calculations, and compare the relative stabilities of the helical spiral and collinear spin structures of CuFeO\(_2\) and
AgCrO$_2$ on the basis of the calculated spin exchange constants. As for the origin of the FE polarizations in the helical spiral-spin order states of CuFeO$_2$ $^{22}$ and AgCrO$_2$, $^{23}$ only the symmetry of the spin arrangement in their MO$_2$ ($M = Fe, Cr$) layers was analyzed to find that when the pattern of the spin arrangement has, for example, a $C_2$ or $C'_2$ symmetry axis, the FE polarization is along this axis. However, such symmetry analyses cannot predict whether the FE polarization should be pointed along the positive or negative direction of the rotational symmetry axis and how the polarization direction depends on the sense of the helical rotation (left- or right-handed rotation). The loss of inversion symmetry brought about by the helical spiral-spin order will induce asymmetric electron density distribution on some atoms of CuFeO$_2$ (likewise, AgCrO$_2$). It is of interest to know which atoms are largely responsible for the asymmetric density distribution causing the FE polarization and how such local electron density distributions are related to the direction of the FE polarization. In the present work, these questions concerning CuFeO$_2$ and AgCrO$_2$ were investigated on the basis of density functional calculations.

2. Details of calculations

Our spin-polarized DFT calculations employed the projector augmented wave method $^{40,41}$ coded in the Vienna $ab$ initio simulation package, $^{42}$ the generalized gradient approximation (GGA) for the exchange and correlation corrections, $^{43}$ and the plane wave cutoff energies of 500 and 400 eV for the calculations without and with SOC, respectively. To describe the electron correlation associated with the Fe 3d states, the GGA plus on-site repulsion U (GGA+U) method was applied with an effective $U = 4$ eV on the Fe atom. As in
the case of AgCrO$_2$,$^23$ we consider the four spin exchange interactions J$_1$ – J$_4$ defined in Fig. 4.1 and evaluate their values by performing GGA+U calculations for the five ordered spin states of CuFeO$_2$ defined in Fig. 4.3.

For the ferroelectricity driven by a chiral magnetic order, it is essential to take into consideration SOC effects in electronic structure calculations.$^{17-22}$ To estimate the FE polarization of CuFeO$_2$ under magnetic field, we performed GGA+U+SOC calculations for three model helical spiral-spin states of CuFeO$_2$ (see Section 5) and subsequently calculated the associated FE polarizations by using the Berry phase method.$^{44,45}$ In these Berry phase calculations, we employed a (3a,3b,2c) supercell.

3. Spin exchange interactions

We determine the four spin exchange parameters J$_1$ – J$_4$ of CuFeO$_2$ (Fig. 4.1) by performing mapping analysis on the basis of the five ordered spin states (FM, AF1, AF2, AF3, AF4) shown in Fig. 4.3. The relative energies, per three formula units (FUs), of these states were determined from our GGA+U calculations as summarized in Fig. 4.3. The energies of these states can also be described in terms of the spin Hamiltonian,

$$\hat{H} = -\sum_{i<j} J_{ij} \hat{S}_i \cdot \hat{S}_j,$$

where J$_{ij}$ (= J$_1$ – J$_4$) is the spin exchange parameter for the spin exchange interaction between the spin sites i and j. By applying the energy expressions obtained for spin dimers with N unpaired spins per spin site (N = 5 for CuFeO$_2$),$^{46,47}$ the total spin exchange energies of the five ordered spin states (per three FUs) are written as summarized in Fig. 4.3. Thus, by
mapping the relative energies of the five ordered spin states determined by the GGA+U calculations onto the corresponding relative energies determined from the above spin exchange energies, we obtain the values of $J_1 - J_4$ summarized in Fig. 4.1c, where the corresponding values of AgCrO$_2$ are also listed for comparison. (To compare the spin exchange interactions of CuFeO$_2$ with those of AgCrO$_2$, it is necessary to use the effective spin exchanges $J_i^{\text{eff}} = S^2 J_i$, where $S = 5/2$ and 3/2 for CuFeO$_2$ and AgCrO$_2$, respectively.)

Fig. 4.1c shows that the intra-layer exchanges $J_1$ and $J_2$ as well as the inter-layer exchange $J_4$ of CuFeO$_2$ are substantially antiferromagnetic (AFM). In each FeO$_2$ layer, spin frustration occurs in the $(J_1, J_1, J_1)$ and $(J_2, J_2, J_2)$ triangles and in the $(J_1, J_1, J_2)$ line segments. Between adjacent FeO$_2$ layers, spin frustration occurs in the isosceles $(J_1, J_4, J_4)$ triangles. Namely, both the intra-layer and the inter-layer interactions are spin-frustrated in CuFeO$_2$, as found for AgCrO$_2$. The spin exchange interactions of CuFeO$_2$ differ from those of AgCrO$_2$ in two aspects: (a) Among $J_1 - J_4$, the AFM inter-layer spin exchange $J_4$ is the strongest interaction in AgCrO$_2$ but is quite weak in CuFeO$_2$, and (b) the intra-layer exchange $J_3$ is ferromagnetic (FM) in AgCrO$_2$ but is AFM in CuFeO$_2$. As discussed in the next section, these two differences are important in explaining why a magnetic field applied parallel to the c-axis is necessary for CuFeO$_2$ to adopt the helical spiral-spin structure while this is not the case for AgCrO$_2$.

It is known that GGA+U electronic structure calculations generally overestimate the magnitude of spin exchange interactions. To find the overestimation factors $f$ for the calculated spin exchange parameters of CuFeO$_2$ and AgCrO$_2$ (Fig. 4.1c), we calculate their Curie-Weiss temperatures $\theta$ using the mean field approximation, namely,
\[ \theta = \frac{S(S+1)}{3k_B} \sum_i z_i J_i, \]

where the summation runs over all nearest neighbors of a given spin site, \( z_i \) is the number of nearest neighbors connected by the spin exchange parameter \( J_i \), and \( S \) is the spin quantum number of each spin site (i.e., \( S = 5/2 \) for Fe\(^{3+}\) in CuFeO\(_2\), and \( S = 3/2 \) for Cr\(^{3+}\) in AgCrO\(_2\)).

Thus, for CuFeO\(_2\) and AgCrO\(_2\), \( \theta \) can be approximated by

\[ \theta \approx 2S(S+1)(J_1 + J_2 + J_3 + J_4)/k_B \]

The \( J_1 - J_4 \) values of Fig. 4.1c lead to \( \theta = -292 \) and -283 K for CuFeO\(_2\) and AgCrO\(_2\), respectively, while the corresponding experimental values are -90 \(^{55}\) and -200 K, \(^{56}\) respectively. Therefore, \( J_1 - J_4 \) values are overestimated by \( f = 3.24 \) for CuFeO\(_2\), and by \( f = 1.42 \) for AgCrO\(_2\). Therefore, in estimating the relative stabilities of various ordered spin states of CuFeO\(_2\) and AgCrO\(_2\) in terms of their spin exchange parameters \( J_1 - J_4 \) listed in Fig. 4.1c, we will employ the \( J_1 - J_4 \) values reduced by the overestimation factor \( f \).

4. Relative stabilities of the helical spiral and collinear spin structures

To probe why a magnetic field applied parallel to the c-axis is needed for CuFeO\(_2\) to acquire a helical spiral-spin structure, we first determine the magnetic anisotropy of CuFeO\(_2\) by performing GGA+U+SOC calculations for its ↑↑↓↓ state. These calculations reveal that the spin orientation parallel to the c-axis (∥c) is more stable than that perpendicular to the c-axis (⊥c) by 0.12 meV per FU, namely, the magnetic anisotropy of each Fe\(^{3+}\) (\( S = 5/2 \)) ion is very weak. This is not surprising because, to a first approximation, \( L = 0 \) for the Fe\(^{3+}\) ion in each FeO\(_6\) octahedron so that the effect of SOC should be weak. This suggests that the spin
orientation of CuFeO$_2$ might be easily influenced by extrinsic factors such as oxygen vacancy$^{39}$ and applied magnetic field.

Since CuFeO$_2$ can switch from the $↑↑↓↓$ state to the helical spiral-spin state depending on the strength of applied magnetic field $H < \sim 13$ T, the two states should be close in energy. (Note that 1 T is equivalent to 0.67 K.) Such a field-dependence is not known for AgCrO$_2$, which adopts the helical spiral-spin state, thereby implying that the $↑↑↓↓$ state is much less stable than the helical spiral-spin state in AgCrO$_2$. To verify these implications, we examine the relative stabilities of several helical spiral and collinear spin structures of CuFeO$_2$ and AgCrO$_2$ in terms of their spin exchange parameters $J_1 – J_4$. As a representative example of the helical spiral-spin structure, we consider the helical spiral-spin structure $Q_{a+b} = (q, q)$ as a function of the helical rotation angle $\theta = q \times 360^\circ$ ($q = 1/5, 1/4, 1/3, 1/2$) (see Section 5 for the definition of this helical spiral-spin structure). In terms of $J_1 – J_4$, the energy $E(\theta)$ of the $Q_{a+b}$ structure as a function of $\theta$ is written as

$$E(\theta) = -3J_1[2\cos\theta + \cos 2\theta] - 3J_2[2\cos 2\theta + \cos 4\theta] - 3J_3[1 + 2\cos 3\theta] - J_4[3 + 4\cos \theta + 2\cos 2\theta](N^2/4)$$

(4)

The $E(\theta)$ vs. $\theta$ plots calculated for CuFeO$_2$ and AgCrO$_2$ using their spin exchange parameters (reduced by the overestimation factor $f$) are presented in Fig. 4.4 in the region of $\theta = 60 – 180^\circ$ (i.e., $q = 1/6 – 1/2$).

The $E(\theta)$ vs. $\theta$ curves have the minimum at $\theta = 120^\circ$ (i.e., $q = 1/3$) for both CuFeO$_2$ and AgCrO$_2$. This prediction is in good agreement with experiment for AgCrO$_2$.$^{36,37}$ It should be noted that the potential well around $\theta = 120^\circ$ is deep around $\theta = 120^\circ$ for AgCrO$_2$, but is
very shallow for CuFeO₂. To probe the origin of this difference, we calculate the spin exchange energies of their \( \uparrow\uparrow\downarrow\downarrow \), \( Q_{a+b} \) (q = 1/3, 1/4, 1/5) and \( \uparrow\uparrow\uparrow\downarrow\downarrow \) states in terms of their spin exchange parameters. The results of these calculations, summarized in Table 4.1, reveal that the \( \uparrow\uparrow\downarrow\downarrow \) state is less stable than the \( Q_{a+b} \) (q = 1/3) state in both CuFeO₂ and AgCrO₂. However, the \( \uparrow\uparrow\downarrow\downarrow \) state is much closer in energy to the \( Q_{a+b} \) (q = 1/3) state for CuFeO₂ than for AgCrO₂. According to Table 4.1, the \( Q_{a+b} \) (q = 1/3) state is more stable than the \( \uparrow\uparrow\downarrow\downarrow \) state by

\[
\Delta E = (-0.50J_1 - 0.50J_2 + 2J_3 - 0.33J_4)(N^2/4),
\]

where \( N = 5 \) for CuFeO₂, and \( N = 3 \) for AgCrO₂. Thus, \( \Delta E \) is large for AgCrO₂ due to the strongly AFM \( J_4 \) and the FM \( J_3 \), while \( \Delta E \) is small for CuFeO₂ due to the weakly AFM \( J_4 \) and the AFM \( J_3 \).

Since the \( Q_{a+b} \) (q = 1/3) and \( \uparrow\uparrow\downarrow\downarrow \) states of CuFeO₂ are close in energy, the extrinsic factors such as oxygen vacancy\(^39\) and applied magnetic field might easily affect which state CuFeO₂ adopts. It has been suggested that an O vacancy in a FeO₂ layer creates Fe\(^{2+}\) ions at the FeO₂ square pyramids around the vacancy site, and the uniaxial magnetism of such Fe\(^{2+}\) ions\(^39,57\) provides a driving force for the surrounding Fe\(^{3+}\) ions to orient their moments along the c-axis leading to the \( \uparrow\uparrow\downarrow\downarrow \) state. An applied magnetic field tends to orient the moment of a magnetic ion perpendicular to the field when the field is not strong so that the Zeeman levels of the ion are almost equally populated. Thus, under such magnetic field applied along the c-axis, the spin orientation of CuFeO₂ would be governed by two competing factors; the oxygen-vacancy effect favoring the //c-spin orientation and the magnetic-field effect favoring
the \( \perp \)c-spin orientation. Then, the adoption of the helical spiral-spin structure under magnetic field \( H \approx 7 - 13 \) T implies that the magnetic-field effect overcomes the oxygen-vacancy effect, so the intra- and interlayer spin frustration of CuFeO\(_2\) is reduced by adopting the helical spiral-spin structure, as found for AgCrO\(_2\). The occurrence of the \( \uparrow \uparrow \uparrow \downarrow \downarrow \) structure under \( H > \sim 13 \) T suggests that the energy gap between adjacent Zeeman levels of the Fe\(^{3+}\) ion become large, so only the lower-lying Zeeman levels are preferentially populated thereby resulting in more moments parallel to the field direction.

5. Ferroelectric polarization

Arima considered two types of helical spiral-spin order in CuFeO\(_2\) that lead to FE polarization along the direction in the ab-plane\(^2\), one with the propagation vector \((q, q)\) along the \((a+b)\) direction and the other with the propagation vector \((0, q)\) perpendicular to the a-axis. The reported \( q \) is about \( 1/5 < q < 1/4 \), for which the helical rotation angle ranges between \( 72^\circ \) and \( 90^\circ \). Such \( q \) values gives rise to a repeat unit cell too large for our GGA+U+SOC calculations, so we use \( q = 1/3 \) (i.e., the helical-rotation angle of \( 120^\circ \)) to simplify our calculations. As presented in Fig. 4.5, we consider the three helical spiral-spin structures described by the propagation vectors \( Q_a = (1/3, 0) \), \( Q_{\perp a} = (0, 1/3) \), and \( Q_{a+b} = (1/3, 1/3) \). In \( Q_a \) and \( Q_{a+b} \) the helical spiral-spin chains run along the positive a-direction with clockwise helical-rotation of \( 120^\circ \). In \( Q_a \) the spiral-spin chains repeat along the b-direction without changing the rotational angle (Fig. 4.5a). In \( Q_{a+b} \), the spiral-spin chains repeat along the positive b-direction while advancing the helical-rotation clockwise by \( 120^\circ \) (Fig. 4.5c).
the helical spiral-spin chains run along the positive (a+b)- and the positive b-direction with the helical-rotational plane perpendicular to the $\perp a$-axis (Fig. 4.5b).

For the $Q_a$, $Q_{\perp a}$, and $Q_{a+b}$ states, GGA+U calculations do not show FE polarization, but GGA+U+SOC calculations do. The calculated values of the FE polarization $P$ are comparable to the experimental values so that the SOC effect is essential for the FE polarization, as found for other multiferroic systems induced by magnetic order.\textsuperscript{17-21} In $Q_{\perp a}$ state, the FE polarization is along the positive $a$-direction with $P = 216 \ \mu$C/m$^2$. This result confirms Arima’s prediction for the case of the ($0$, $q$) propagation,\textsuperscript{22} which has $C_2$-rotational symmetry along the $a$-direction. In the $Q_{a+b}$ state, the FE polarization is along the positive $a$-direction with $P = 84 \ \mu$C/m$^2$. Given the equivalence of the (a+b)- and a-directions, this result confirms Arima’s prediction for the case of the ($q$, $q$) propagation,\textsuperscript{22} for which the magnetic structure has $C_2'$ symmetry along the $a$-direction (i.e., $C_2$ rotation followed by time reversal) (Fig. 4.5c). In the $Q_a$ state, the FE polarization is nonzero along the $\perp (a+b)$-direction in the ab-plane (see Fig. 4.5a), i.e., $P_{\perp(a+b)} = 219 \ \mu$C/m$^2$, and also along the positive $c$-direction, i.e., $P_{/c} = 138 \ \mu$C/m$^2$. The magnetic structure of the $Q_a$ state has no global symmetry but give rise to a nonzero FE polarization, as similarly found for AgCrO$_2$.\textsuperscript{23} The cause for this observation has been explained on the basis of the hidden mirror-plane symmetry of the spin arrangement in each CrO$_4$ chain along the (a+b)-direction.\textsuperscript{23}

Let us now examine the absolute direction of the FE polarization for cases when the polarization is along the $C_2$ axis in the $Q_{\perp a}$ state or along the $C_2'$ axis in the $Q_{a+b}$ state. To help understand the asymmetric electron density distribution brought about by SOC and
hence leading to the FE polarization, we calculate the difference electron density $\Delta \rho(r) = \rho(r) - \rho_0(r)$, where $\rho(r)$ is the electron density obtained from the GGA+U+SOC calculations, and $\rho_0(r)$ is that from the GGA+U calculations. We analyze the difference density $\Delta \rho(r)$ by constructing isosurface plots for various values of $\Delta \rho(r)$, to find that the asymmetric density distribution responsible for the FE polarization occurs primarily around the O atoms for the $\Delta \rho(r)$ values in the region of $-0.06 \sim -0.04$ e$^-$/Å$^3$. The plots of $\Delta \rho(r)$ calculated for the helical spiral-spin state $Q_{\perp a}$ are presented in Fig. 4.6. The three-dimensional isosurface plot in Fig. 4.6a shows that the asymmetric electron density distribution causing the FE polarization occurs mainly around the O atoms. The cross-section views of $\Delta \rho(r)$ on the two O atom sheets of a FeO$_2$ layer are presented in Fig. 4.6b, where each O atom creates a dipole moment around it. In each sheet of the O atoms, the dipole directions are identical at all O atoms. However, the two O atom sheets are different in the dipole directions, and the FE-polarization direction is given by the vector sum of the two dipole directions. In terms of the convention that the positive dipole direction is from the lower to the higher electron density region (e.g., $\delta^+ \rightarrow \delta^-$), the $Q_{\perp a}$ state with right-handed-helical rotation going along the positive (a+b)- and the positive b-directions has the FE polarization pointed along the positive a-direction. Though not shown, when the helical-rotation direction is left-handed, the FE polarization is pointed along the negative a-direction. We also analyzed the difference density $\Delta \rho(r)$ for the $Q_{a+b}$ state with right-handed-helical rotation going along the positive a-direction to find that its FE polarization is pointed along the positive a-direction, and the FE polarization is reversed when the helical-rotation is left-handed.
6. Concluding remarks

The spin exchanges of CuFeO₂ are frustrated, as found for AgCrO₂, but the two systems differ; the AFM inter-layer exchange J₄ is strong in AgCrO₂ but weak in CuFeO₂, and the intra-layer exchange J₃ is FM in AgCrO₂ but AFM in CuFeO₂. In contrast to the case of AgCrO₂, therefore, the ↑↑↓↓ state is only slightly higher in energy than the helical spiral-spin state Qₐ+b (q = 1/3) in CuFeO₂ so that extrinsic factors such as oxygen vacancy and applied magnetic field can influence whether it adopts the ↑↑↓↓ or Qₐ+b (q = 1/3) structure. The magnitudes of the FE polarization calculated for the model helical spiral-chain structures of CuFeO₂ are in good agreement with experiment. The FE polarization of CuFeO₂ arises largely from the asymmetric electron density distributions around the oxygen atoms, and the polarization direction is related to the associated dipole directions and to the handedness of the helical spin rotation.

Acknowledgments

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(7) Tokura, Y. Science 2006, 312, 1481.


Table 4.1. Spin exchange energies (per FU) of the \( \uparrow\downarrow\downarrow\downarrow \), \( Q_{a+b} \) (q = 1/3, 1/4, 1/5) and \( \uparrow\uparrow\uparrow\downarrow\downarrow \) states of CuFeO\(_2\) and AgCrO\(_2\) in terms of their spin exchange parameters \( J_1 \) – \( J_4 \).

<table>
<thead>
<tr>
<th>State</th>
<th>Energy expression (per FU)(^a)</th>
<th>CuFeO(_2) meV/FU</th>
<th>AgCrO(_2) meV/FU</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \uparrow\downarrow\downarrow\downarrow )</td>
<td>( (J_1 + J_2 - J_3 - 0.33J_4)(N^2/4) )</td>
<td>-1.58 (^b)</td>
<td>-2.94 (^c)</td>
</tr>
<tr>
<td>( Q_{a+b} ) (q = 1/3)</td>
<td>( (1.50J_1 + 1.50J_2 - 3J_3)(N^2/4) )</td>
<td>-2.17</td>
<td>-7.01</td>
</tr>
<tr>
<td>( Q_{a+b} ) (q = 1/4)</td>
<td>( (J_1 + J_2 - J_3 - 0.33J_4)(N^2/4) )</td>
<td>-1.58</td>
<td>-2.94</td>
</tr>
<tr>
<td>( Q_{a+b} ) (q = 1/5)</td>
<td>( (0.19J_1 + 1.31J_2 + 0.62J_3 - 0.87J_4)(N^2/4) )</td>
<td>-0.77</td>
<td>+0.88</td>
</tr>
<tr>
<td>( \uparrow\uparrow\uparrow\downarrow\downarrow )</td>
<td>( (0.20J_1 + J_2 + 0.20J_3 - 0.87J_4)(N^2/4) )</td>
<td>-0.49</td>
<td>+0.94</td>
</tr>
</tbody>
</table>

\(^a\) \( N = 5 \) for CuFeO\(_2\), and \( N = 3 \) for AgCrO\(_2\).

\(^b\) Using the \( J_1 \) – \( J_4 \) values reduced by the overestimation factor \( f = 3.24 \) (see the text).

\(^c\) Using the \( J_1 \) – \( J_4 \) values reduced by the overestimation factor \( f = 1.42 \) (see the text).
Figure 4.1. (a) An isolated FeO$_2$ layer of CuFeO$_2$ made of edge-sharing FeO$_6$ octahedra showing the intra-layer spin exchange paths J$_1$, J$_2$ and J$_3$. (b) A zoomed-in view of how two adjacent FeO$_2$ layers of CuFeO$_2$ are linked by O-Cu-O bridges showing the inter-layer spin exchange J$_4$. The Fe, Cu, and O atoms are indicated by red, blue and white circles, respectively. The numbers 1 – 4 in (a, b) refer to the spin exchange paths J$_1$ – J$_4$, respectively. (c) The values of J$_1$ – J$_4$ (in meV) found for CuFeO$_2$ and AgCrO$_2$ obtained from GGA+U+SOC calculations.
Figure 4.2. The collinear magnetic structures of CuFeO₂ below 10 K under magnetic field: (a) the $↑↑↓↓$ structure under magnetic field lower than $\sim 7$ T and (b) the $↑↑↑↓↓$ structure under magnetic field greater than $\sim 13$ T. The filled and empty circles represent the spins of the Fe$^{3+}$ ions are aligned along the positive and negative c-axis directions, respectively.
Figure 4.3. Five ordered spin states of CuFeO$_2$ constructed by using a (3a, 2b, c) supercell, where the filled and empty circles represent up-spin and down-spin Fe$^{3+}$ sites, respectively. In (a – d), all three FeO$_2$ layers of the (3a, 2b, c) supercell have the same spin arrangement, so that the spin arrangement of only one FeO$_2$ layer is shown. In (e), the spins are ferromagnetic in each FeO$_2$ layer, but the (3a, 2b, c) supercell consists of one up-spin and two down-spin layers. For each state, the number in each square bracket refers to the relative energy per three FUs determined from GGA+U calculations, and the energy expression to the total spin exchange energy per three FUs with N = 5.

<table>
<thead>
<tr>
<th>State</th>
<th>Energy (eV)</th>
<th>Energy Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>FM</td>
<td>91.0</td>
<td>$(-9J_1-9J_2-9J_3-9J_4)N^2/4$</td>
</tr>
<tr>
<td>AF1</td>
<td>10.5</td>
<td>$(+3J_1-9J_2+3J_3-J_4)N^2/4$</td>
</tr>
<tr>
<td>AF2</td>
<td>19.6</td>
<td>$(-J_1-J_2+3J_3-11J_4/3)N^2/4$</td>
</tr>
<tr>
<td>AF4</td>
<td>0.0</td>
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</tr>
<tr>
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Figure 4.4. Plots of the spin exchange energy $E(\theta)$, per FU, of the helical spiral-spin structure $Q_{a+b} = (q, q)$ calculated as a function of the helical rotation angle $\theta = q \times 360^\circ$ for CuFeO$_2$ and AgCrO$_2$ by using their spin exchange parameters $J_1 - J_4$ reduced by the overestimation factor $f = 3.24$ for CuFeO$_2$, and by $f = 1.42$ for AgCrO$_2$. 
Figure 4.5. Three magnetic states of CuFeO$_2$ generated by using helical spiral-spin chains: (a) $Q_a$, (b) $Q_{\perp a}$, and (c) $Q_{a+b}$. The number 0, 1 and -1 in the FeO$_6$ octahedra show that the helical-rotation angles of 0°, 120° and -120°, respectively, in the helical rotation-planes (short solid black line). (d) Three directions along which there occur FeO$_4$ chains of edge-sharing FeO$_6$ octahedra. The calculated FE polarization is along the a-direction with $P = 216$ $\mu$C/m$^2$ for $Q_{\perp a}$, and along the a-direction with $P = 84$ $\mu$C/m$^2$ for $Q_{a+b}$. The FE polarization vector $\vec{P}$ for $Q_a$ does not lie in the ab-plane with $P_{\perp (a+b)} = 219$ $\mu$C/m$^2$) and $P_{//c} = 138$ $\mu$C/m$^2$. 
Figure 4.6. Plots of the difference charge density $\Delta\rho(r)$ calculated for the helical spiral-spin state $Q_{\perp a}$: (a) The three-dimensional isosurface plot showing the successive sheets of the Cu, O, Fe, O and Cu atoms, where the value for the isodensity surface is $-0.05 \, e^-/\AA^3$. (b) The cross-section views of $\Delta\rho(r)$ on the two O atom sheets of a FeO$_2$ layer (covering the $\Delta\rho(r)$ values between $-0.06$ and $-0.04 \, e^-/\AA^3$), where the upper- and lower planes are given on the top and bottom panels, respectively, and the small red and white circles represent the Fe and O atoms, respectively. The red and blue colors represent the $\Delta\rho(r)$ values of $-0.06$ and $-0.04 \, e^-/\AA^3$, respectively. Thus, the larger and smaller red-regions at each O site refer to a more and less depleted electron density regions, respectively. Given the convention that the positive dipole direction is from the less electron density toward the more electron density ($\delta^+ \rightarrow \delta^-$), the local dipole direction at each O atom is from the larger to the smaller red-regions, as represented by the red arrows.
CHAPTER 5

Density functional analysis of the spin exchange interactions and charge order patterns in the layered magnetic oxides YBaM$_2$O$_5$ (M = Mn, Fe, Co)

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Yuemei Zhang and Myung-Hwan Whangbo*

Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204, USA

Abstract

The spin and charge order phenomena of the layered magnetic oxides YBaM$_2$O$_5$ (M = Mn, Fe, Co) were analyzed on the basis of density functional calculations. We evaluated the spin exchange interactions of YBaM$_2$O$_5$ by performing energy-mapping analysis based on density functional calculations to find why they undergo a three-dimensional magnetic ordering at high temperature. We estimated the relative stabilities of the checkerboard and stripe charge order patterns of YBaM$_2$O$_5$ (M = Mn, Fe, Co) by optimizing their structures with density functional calculations to probe if the nature of the charge order pattern depends on whether their transition-metal ions Jahn-Teller active.

Email: mike_whangbo@ncsu.edu
1. Introduction

Transition-metal oxides based on perovskite-type structures exhibit rich physical properties associated with the charge, spin and/or orbital order of their transition-metal cations. The layered magnetic oxides $\text{YBaM}_2\text{O}_5$ ($\text{M} = \text{Mn, Fe, Co}$) are quite special because they exhibit all three types of ordering phenomena. In the $\text{M}_2\text{O}_5$ slabs of $\text{YBaM}_2\text{O}_5$, the $\text{MO}_5$ square pyramids form the $\text{M}_2\text{O}_9$ dumbbell units by sharing their apical O atoms ($\text{O}_{\text{ap}}$) and these dumbbell units share their basal O atoms ($\text{O}_{\text{bs}}$) to form the $\text{M}_2\text{O}_5$ slabs parallel to the ab-plane. These slabs, containing a $\text{Ba}^{2+}$ ion in every $\text{M}_4$ cube, alternate with layers of $\text{Y}^{3+}$ ions along the c-direction (Fig. 5.1). The transition-metal ions exist as $\text{M}^{2.5+}$ cations when their sites are equivalent in structure. This mono-valence state of $\text{YBaM}_2\text{O}_5$ is stable at high temperatures, but lowering the temperature induces a charge order (i.e., charge disproportionation), $2 \text{M}^{2.5+} \rightarrow \text{M}^{2+} + \text{M}^{3+}$, leading to a mixed-valence state. Two different types of charge order occur in the $\text{M}_2\text{O}_5$ slabs of $\text{YBaM}_2\text{O}_5$; $\text{YBaMn}_2\text{O}_5$ exhibits a checkerboard charge order (CCO) of the $\text{M}^{2+}$ and $\text{M}^{3+}$ ions (Fig. 5.2a), whereas both $\text{YBaFe}_2\text{O}_5$ and $\text{YBaCo}_2\text{O}_5$ show a stripe charge order (SCO) of the $\text{M}^{2+}$ and $\text{M}^{3+}$ ions with the stripes running along the b-direction (Fig. 5.2b). $\text{YBaMn}_2\text{O}_5$ is similar to $\text{YBaM}_2\text{O}_5$ ($\text{M} = \text{Fe, Co}$) in spin order in that their magnetic ground states adopt a G-type antiferromagnetic (AFM) coupling between nearest-neighbor spins along the a-, b- and c-directions. Nevertheless, the SCO plus the G-type AFM spin order leads to zero overall moment (i.e., AFM state) for $\text{YBaM}_2\text{O}_5$ ($\text{M} = \text{Fe, Co}$), but the CCO plus the G-type AFM spin order to a nonzero overall moment (i.e., ferrimagnetic state) for $\text{YBaMn}_2\text{O}_5$. Furthermore,
YBaMn$_2$O$_5$ is different from YBaM$_2$O$_5$ (M = Fe, Co) in that the spin orientation is along the c-axis in YBaMn$_2$O$_5$, but perpendicular to the c-axis in YBaM$_2$O$_5$ (M = Fe, Co).\textsuperscript{4,5}

Due to their interesting physical properties, the layered oxides YBaM$_2$O$_5$ (M = Mn, Fe, Co) have been examined in a number of theoretical studies based on density functional theory (DFT) calculations.\textsuperscript{6-13} Vidya et al.\textsuperscript{8} found the ferrimagnetic state to be the ground state for YBaMn$_2$O$_5$, and showed the occurrence of the orbital order associated with the CCO in terms of charge-density plots. Xiang et al.\textsuperscript{10} showed that the nature of the magnetic ground state of YBaMn$_2$O$_5$ depends on the $\angle$Mn-O-Mn angle of the Mn-O-Mn bridges in the ab plane. Hap et al.\textsuperscript{11} examined YBaFe$_2$O$_5$ to show that the orbital order corresponds to the local distortions of the FeO$_5$ square pyramids. Vidya et al.\textsuperscript{12} confirmed the ferrimagnetic ground state for YBaMn$_2$O$_5$ and the G-type AFM ground states for YBaFe$_2$O$_5$ and YBaCo$_2$O$_5$, and analyzed the Born effective charges to assess the charge orders of YBaM$_2$O$_5$ (M = Mn, Fe, Co). Using a model Hamiltonian and the assumption that the crystal field split pattern, (xz, yz) < xy < $z^2$ < $x^2$-$y^2$, for a MO$_5$ square pyramid with C$_{4v}$ symmetry, Wang et al.\textsuperscript{14} investigated the relative stabilities of the CCO and SCO in YBaMn$_2$O$_5$ and YBaCo$_2$O$_5$ to suggest that the CCO is favored when there is no Jahn-Teller (JT) active ion, but the SCO is favored if there exist JT-active ions.

There are two aspects of YBaM$_2$O$_5$ (M = Mn, Fe, Co) that remain puzzling. One is that their three-dimensional (3D) magnetic ordering temperatures are high; the 3D AFM ordering of YBaFe$_2$O$_5$ and YBaCo$_2$O$_5$ occurs at high temperatures (at $T_N = 430$\textsuperscript{4} and 330 K,\textsuperscript{5} respectively), and so is the ferromagnetic ordering of YBaMn$_2$O$_5$ (167 K).\textsuperscript{2} This implies that the M-O…O-M (M = Mn, Fe, Co) spin exchange interactions between adjacent M$_2$O$_5$ slabs
along the c-axis is substantially strong. So far, there has been no systematic study on the spin exchange interactions of all three oxides YBaM$_2$O$_5$ (M = Mn, Fe, Co). In the neutron scattering study of YBaFe$_2$O$_5$ by Chang et al.,$^{15}$ the strength of the inter-slab Fe-O…O-Fe spin exchange was estimated to be only 1 % of the Fe-O-Fe spin exchange within each Fe$_2$O$_9$ dumbbell.$^{15}$ Spiel et al.$^{13}$ extracted a few spin exchange parameters of YBaFe$_2$O$_5$ from their DFT calculations to compare with the experimental values of Chang et al.,$^{15}$ and reported only the average of the Fe-O…O-Fe and the Fe-O-Fe spin exchanges along the c-direction. Thus, it is timely and important to provide a comprehensive study of the spin exchange interactions for all YBaM$_2$O$_5$ (M = Mn, Fe, Co) on the basis of DFT calculations. The other puzzling aspect is if the nature of the charge order pattern of YBaM$_2$O$_5$ is determined by whether their M$^{2+}$ and/or M$^{3+}$ ions are JT-active or not. The crystal field split pattern, (xz, yz) < xy < z$^2$ < x$^2$-y$^2$, employed by Wang et al.$^{14}$ for a MO$_5$ square pyramid with C$_{4v}$ symmetry is appropriate only if the $\angle$O$_{ap}$-M-O$_{bs}$ angles of the MO$_5$ square pyramids are close to 90$^\circ$.$^{16}$ In YBaM$_2$O$_5$ (M = Mn, Fe, Co) these angles are substantially greater than 90$^\circ$, which lowers the xy level below the (xz, yz) level, leading to the split pattern xy < (xz, yz) < z$^2$ < x$^2$-y$^2$. As a consequence, the high-spin Mn$^{2+}$ and Mn$^{3+}$ ions of YBaMn$_2$O$_5$ are not JT-active, nor are the high-spin Fe$^{2+}$ and Fe$^{3+}$ ions of YBaFe$_2$O$_5$. Nevertheless, the CCO is found in YBaMn$_2$O$_5$, but the SCO in YBaFe$_2$O$_5$. Thus, it is questionable if the model Hamiltonian study of Wang et al.$^{14}$ is valid. It is important to quantitatively estimate the relative stabilities of the CCO and SCO in each of YBaM$_2$O$_5$ (M = Mn, Fe, Co) on the basis of DFT calculations.
In the present work the aforementioned two questions are investigated. We evaluate the spin exchange interactions of all three oxides YBaM$_2$O$_5$ (M = Mn, Fe, Co) by performing energy-mapping analysis based on DFT calculations. Then we estimate the relative stabilities of the CCO and SCO in YBaM$_2$O$_5$ (M = Mn, Fe, Co) by optimizing their structures in their magnetic ground state on the basis of DFT calculations.

2. Details of calculations

Our spin-polarized density functional calculations employed the projector augmented wave method encoded in the Vienna *ab initio* simulation package, the generalized gradient approximation for the exchange and correlation corrections, and the plane wave cutoff. The electron correlation associated with the M 3d states was taken care of by performing DFT plus on-site repulsion (DFT+U) calculations. The DFT+U method is empirical in nature because one needs to determine the U value appropriate for a given magnetic system by performing a series of DFT+U calculations with several different U values. For the YBaM$_2$O$_5$ (M = Mn, Fe, Co) system, the most important magnetic property to reproduce by DFT+U calculations is that they all adopt the G-type AFM spin arrangement as the magnetic ground state. The U value typically used for the transition-metal elements Mn, Fe, Co and Cu is in the vicinity of 4 eV. For YBaFe$_2$O$_5$ and YBaCo$_2$O$_5$, the G-type AFM state is found to be the magnetic ground state by using U = 4 eV. For YBaMn$_2$O$_5$, however, the ferrimagnetic state resulting from the G-type AFM spin coupling is not the magnetic ground state if the U value is greater than ∼1 eV (see Fig. 5.2 and Table 5.1). A similar situation was found for the magnetic oxide Ca$_3$CoMnO$_6$, which consists of trigonal
arrangement of the CoMnO₆ chains made up of face-sharing CoO₆ trigonal prisms and MnO₆ octahedra; the magnetic ground state that has the ↑↑↓↓ spin arrangement of the Co²⁺ and Mn⁴⁺ ions is not reproduced by DFT+U calculations if the U value for Mn is greater than 1 eV. Thus, in the present DFT+U calculations, we employed U = 1 eV for YBaMn₂O₅ and U = 4 eV for YBaFe₂O₅ and YBaCo₂O₅.

3. Evaluation of spin exchange interactions

To examine why YBaM₂O₅ (M = Mn, Fe, Co) adopts the G-type AFM spin coupling, we evaluate the spin exchange parameters J₁ – J₉ for YBaMn₂O₅ defined in Fig. 5.3a, and J₁ – J₁₂ for YBaFe₂O₅ and YBaCo₂O₅ defined in Fig. 5.3b, by performing energy-mapping analysis based on DFT+U calculations. For this purpose, we first determine the relative energies of YBaMn₂O₅ for the ordered spin states listed in Fig. 5.4, and those of YBaM₂O₅ (M = Fe, Co) for the ordered spin states listed in Fig. 5.5. The relative energies of these states obtained from the DFT+U calculations are summarized in Table 5.2.

In extracting N spin exchange parameters, the minimum number of ordered spin states needed in the mapping analysis is N+1, which leads one-to-one mapping between the relative energy differences and the spin exchange parameters. For cases dealing with magnetic systems containing mixed-valence magnetic ions, there can be several different sets of N+1 ordered spin states leading to slightly different values for the spin exchange parameters. In such cases, it is more reasonable to employ more ordered spin states than required for one-to-one mapping and carry out mapping analysis on the basis of least-squares fitting.²⁷
The total spin exchange energies of the ordered spin states can be written in terms of the spin Hamiltonian,

\[ \hat{H} = -\sum_{i<j} J_{ij} \hat{S}_i \cdot \hat{S}_j, \quad (1) \]

in which \( J_{ij} (= J_1 - J_9 \text{ for } \text{YBaMn}_2\text{O}_5 \text{ and } J_1 - J_{12} \text{ for } \text{YBaFe}_2\text{O}_5 \text{ and } \text{YBaCo}_2\text{O}_5) \) is the spin exchange parameter for the interaction between the spin sites \( i \) and \( j \) in \( \text{YBaM}_2\text{O}_5 \). In writing the expression for the total spin exchange energy of an ordered spin state, we employ the energy expressions for the ferromagnetic (FM) and AFM arrangements of a general spin dimer whose spin sites \( i \) and \( j \) possess \( N_i \) and \( N_j \) unpaired spins (hence, spins \( S_i = N_i/2 \) and \( S_j = N_j/2 \)), respectively.\(^{28,29}\) Given \( J_{ij} \) as the spin exchange parameter for this spin dimer, the energies of the FM and AFM arrangements of this spin dimer (\( E_{\text{FM}} \) and \( E_{\text{AFM}} \), respectively) are expressed as

\[ E_{\text{FM}} = -N_i N_j J_{ij}/4 = -S_i S_j J_{ij} \]
\[ E_{\text{AFM}} = +N_i N_j J_{ij}/4 = +S_i S_j J_{ij} \quad (2) \]

(Note that \( S = 5/2 \) and \( 2 \) for the high-spin \( \text{Mn}^{2+} \) and \( \text{Mn}^{3+} \) ions, respectively, \( S = 2 \) and \( 5/2 \) for the high-spin \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) ions, respectively, and \( S = 3/2 \) and \( 2 \) for the high-spin \( \text{Co}^{2+} \) and \( \text{Co}^{3+} \) ions, respectively, in \( \text{YBaM}_2\text{O}_5 \).) The total spin exchange energy \( E_{\text{spin}} \) per formula unit (FU) of an ordered spin arrangement, obtained by summing up all pair-wise interactions, can be expressed as

\[ E_{\text{spin}} = \sum_i C_i J_i = C_1 J_1 + C_2 J_2 + C_3 J_3 + \ldots, \quad (3) \]

where \( C_i \) is the coefficient for the spin exchange parameter \( J_i \). The \( C_i \) values for the various
ordered spin states for YBaMn$_2$O$_5$ are summarized in Table S5.1, those for YBaFe$_2$O$_5$ in Table S5.2, and those for YBaCo$_2$O$_5$ in Table S5.3. In mapping the relative energies of the ordered spin states determined from the DFT+U calculations onto the corresponding energies expected from the total spin exchange energies, we carry out least squares fitting analyses. The resulting spin exchange parameters of YBaM$_2$O$_5$ (M = Mn, Fe, Co) are summarized in Table 5.3.

For YBaMn$_2$O$_5$ the three strongest spin exchanges J$_1$, J$_2$ and J$_3$ are AFM and lead to the ferrimagnetic spin arrangement, as found experimentally. For YBaM$_2$O$_5$ (M = Fe, Co), the five strongest spin exchanges J$_1$, J$_2$, J$_4$, J$_5$ and J$_6$ are AFM and lead to the G-type AFM spin arrangement, in agreement with experiment. We note that J$_1$ and J$_3$ of YBaMn$_2$O$_5$ as well as J$_1$, J$_4$, J$_5$ and J$_6$ of YBaM$_2$O$_5$ (M = Fe, Co) are M-O-M superexchanges with large $\angle$M-O-M angles. Thus, they are predicted to be strongly AFM, as confirmed from the present calculations.

A few exchange parameters of YBaFe$_2$O$_5$ were deduced in the neutron scattering study of Chang et al. (The notations of their spin exchange parameters correspond to ours as follows: $J_1 = J_{23}^c$, $J_2 = J_{\text{direct}}$, $J_4 = J_{22}^b$, $J_5 = J_{33}^b$, and $J_6 = J_{23}^a$.) By using perturbation theory, Chang et al. estimated the $J_2/J_1$ ratio to be approximately 0.01, so they neglected $J_2$ in their analysis of the spin wave dispersion relations. However, our DFT+U calculations show that the $J_2$ exchanges of YBaM$_2$O$_5$ are quite strong, i.e., $J_2/J_1 = 0.67, 0.61$ and $0.16$ for M = Mn, Fe and Co, respectively. As found in numerous magnetic oxides, these M-O…O-M exchanges between the dumbbells along the c-direction (Fig. 5.6a) are strongly AFM because their O…O contact distances are short [2.800 ($\times$4) Å for YBaMn$_2$O$_5$, 2.753 ($\times$2) and

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2.838 (×2) Å for YBaFe$_2$O$_5$, and 2.796 (×2) and 2.829 (×2) Å YBaCo$_2$O$_5$. Due to the short O…O contacts and the fact the $\angle$O$_{ap}$-M-O$_{bs}$ angles of the MO$_5$ square pyramids are greater than 90°, the magnetic orbitals (e.g., xz and/or yz) of the MO$_5$ square pyramids associated with $J_2$ overlap substantially through their O 2p orbitals (Fig. 5.6b) thereby making $J_2$ strongly AFM. Consequently, the 3D AFM ordering temperatures of YBaFe$_2$O$_5$ and YBaCo$_2$O$_5$ are high (i.e., $T_N = 430^4$ and 330 K, respectively), and the ferrimagnetic ordering temperature of YBaMn$_2$O$_5$ is substantially high as well (i.e., 167 K). Thus, neglecting $J_2$ is not a good approximation.

By introducing another approximation, $J_{23} = (2J_{23}^a + J_{23}^c)/3$, Chang et al. obtained $J_{33}^b \approx -5.9$ meV, $J_{22}^b \approx -3.4$ meV, and $J_{23} \approx -6.0$ meV for YBaFe$_2$O$_5$. These estimates are comparable to the corresponding numbers of our calculations (i.e., -8.7, -8.8 and -6.8 meV, respectively). In their DFT study of YBaFe$_2$O$_5$, Spiel et al. reported that $J_{33}^b = -10.0$ meV, $J_{22}^b = -4.3$ meV, $J_{23}^a = -4.2$ meV, and $\langle J_{23}^c \rangle \equiv (J_{23}^c + J_{dir})/2 = -5.6$ meV. The corresponding $J_{23}^a$ and $\langle J_{23}^c \rangle$ values of our calculations are -4.2 and -9.8 meV, respectively. Thus, the spin exchange parameters of Spiel et al. are comparable to ours.

4. Preferred charge order pattern

We now examine the energetic difference in the charge order patterns of YBaM$_2$O$_5$ (M = Mn, Fe, Co) in their magnetic ground states by performing DFT+U calculations. For this purpose, it is necessary to determine the relative energies of the CCO and SCO patterns of each YBaM$_2$O$_5$ (M = Mn, Fe, Co). For YBaMn$_2$O$_5$, we optimized the experimentally-
observed CCO structure. To obtain its hypothetical SCO structure, we started our optimization using the geometry of the experimentally-observed SCO structure of YBaFe$_2$O$_5$. Our calculations show that the CCO structure is lower in energy than the SCO structure by 144 meV per FU for YBaMn$_2$O$_5$. For YBaFe$_2$O$_5$ and YBaCo$_2$O$_5$, we optimized their experimentally-observed SCO structures. To find their hypothetical CCO structures, we began our optimization using the CCO structure of YBaMn$_2$O$_5$. The SCO structure is calculated to be more stable than the CCO structure by 133 meV per FU for YBaFe$_2$O$_5$, and by 50 meV per FU for YBaCo$_2$O$_5$. All these results are consistent with the experimental observations. The preference for the SCO over the CCO is considerably stronger for YBaFe$_2$O$_5$ than for YBaCo$_2$O$_5$ (133 vs. 50 meV per FU), although JT-active ions are absent in YBaFe$_2$O$_5$ but present in YBaCo$_2$O$_5$. Therefore, the charge order patterns of YBaM$_2$O$_5$ (M = Mn, Fe, Co) are not determined by whether their transition-metal ions are JT-active or not.

5. Concluding remarks

In YBaM$_2$O$_5$ (M = Mn, Fe, Co) the inter-slab M-O…O-M spin exchanges along the c-axis are strongly AFM. This together with the strong AFM intra-slab spin exchanges explains why the 3D AFM ordering in YBaM$_2$O$_5$ (M = Fe, Co) takes place at temperatures well above the room temperature (i.e., $T_N = 430^\text{d}$ and 330 K, respectively) and why the ferrimagnetic ordering temperature of YBaMn$_2$O$_5$ is high (i.e., 167 K). Our calculations show that the observed charge order patterns of YBaM$_2$O$_5$ (M = Mn, Fe, Co) are not determined by whether or not their transition-metal ions are JT-active.
Acknowledgments

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REFERENCES


(17) The $\angle O_{ap}-M-O_{bs}$ angles of the MO$_5$ square pyramids of YBaMn$_2$O$_5$ are considerably greater than $90^\circ$. Namely, $103.7^\circ$ ($\times4$) at the Mn$^{2+}$ site and $98.5^\circ$ ($\times4$) at the Mn$^{3+}$ site in YBaMn$_2$O$_5$; $^3$ $98.7^\circ$ ($\times2$) along the a-axis and $101.5^\circ$ ($\times2$) along the b-axis at the Fe$^{2+}$
site, and 102.7° (×2) along the a-axis and 103.0° (×2) along the b-axis at the Fe$^{3+}$ site in YBaFe$_2$O$_5$;\(^{4}\) 98.1° (×2) along the a-axis and 97.9° (×2) along the b-axis at the Co$^{2+}$ site, and 104.9° (×2) along the a-axis and 105.5° (×2) along the b-axis at the Co$^{3+}$ site in YBaCo$_2$O$_5$.\(^{5}\)


Table 5.1. Relative energies (in meV per FU) of the FM, A-type AFM and G-type AFM spin arrangements (defined in Fig. 5.3) of YBaMn₂O₅ determined from the DFT+U calculations with U = 0, 1 and 2 eV.

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Table 5.2. Relative energies (meV per FU) of various ordered spin states of YBaM$_2$O$_5$ (M = Mn, Fe, Co) determined from the DFT+U calculations.

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Table 5.3. Values of the spin exchange parameters $J_i$ (in meV) of YBaM$_2$O$_5$ ($M = \text{Mn, Fe, Co}$) determined by mapping analysis based on DFT+U calculations.

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Figure 5.1. Perspective view of the crystal structure of YBaM$_2$O$_5$ (M = Mn, Fe, Co), where the red, white, green and yellow circles represent the M, O, Ba and Y atoms, respectively.

Figure 5.2. Three ordered spin arrangements (namely, the FM, A-type AFM and G-type AFM arrangements) of YBaMn$_2$O$_5$ with the CCO pattern employed to determine the U value appropriate for the DFT+U calculations. The Mn$^{3+}$ and Mn$^{2+}$ sites are identified by the grey and white circles, respectively, in the first diagram. The up-spin and down-spin Mn sites are indicated by cyan and white circles, respectively. The G-type AFM arrangement leads to the ferrimagnetic state.
Figure 5.3. Spin exchange paths of YBaM$_2$O$_5$: (a) $M = \text{Mn}$ and (b) $M = \text{Fe}, \text{Co}$. The $M^{3+}$ and $M^{2+}$ ions are represented by large grey and large white circles, respectively. The numbers 1, 2, 3, etc. represent the spin exchanges $J_1$, $J_2$, $J_3$, etc., respectively.
Figure 5.4. Ordered spin arrangements of YBaMn$_2$O$_5$ employed for the extraction of the nine spin exchange parameters $J_1$ – $J_9$. The up-spin and down-spin Mn sites are indicated by cyan and white circles, respectively. The Mn$^{3+}$ and Mn$^{2+}$ sites are identified by the grey and white circles, respectively, in the first diagram.
Figure 5.5. Ordered spin arrangements of YBaM$_2$O$_5$ (M = Fe, Co) employed for the extraction of the nine spin exchange parameters $J_1$ – $J_{12}$. The up-spin and down-spin M sites are indicated by cyan and white circles, respectively. The $M^{3+}$ and $M^{2+}$ sites are identified by the grey and white circles, respectively, in the first diagram.
Figure 5.6. (a) Two MO$_5$ square pyramids associated with the M-O…O-M spin exchange $J_2$ of YBaM$_2$O$_5$ (M = Mn, Fe, Co), where the M$^{3+}$ and M$^{2+}$ sites are identified by the grey and white circles, respectively. (b) Magnetic orbitals (xz and/or yz) of the two MO$_5$ square pyramids enhancing the strength of the AFM spin exchange $J_2$. 
Supporting information

Table S5.1. Coefficients $C_i$ of the spin exchange parameters $J_i$ in the total spin exchange energy per FU, $E_{\text{spin}} = \sum_i C_i J_i$, for the various ordered spin states of YBaMn$_2$O$_5$ defined in Fig. 5.4.

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Table S5.2. Coefficients $C_i$ of the spin exchange parameters $J_i$ in the total spin exchange energy per FU, $E_{\text{spin}} = \sum_i C_i J_i$, for the various ordered spin states of YBaFe$_2$O$_5$ defined in Fig. 5.5.

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Table S5.3. Coefficients $C_i$ of the spin exchange parameters $J_i$ in the total spin exchange energy per FU, $E_{\text{spin}} = \sum_i C_i J_i$, for the various ordered spin states of YBaCo$_2$O$_5$ defined in Fig. 5.5.

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The magnetic and electronic properties of several magnetic oxides of transition-metal elements were investigated by examining their spin exchange interactions and SOC effect on the basis of first-principles DFT calculations. In our study, we interpreted the results from these calculations in terms of orbital interactions.

In Ca$_3$CoMnO$_6$, the phenomena of JT instability, uniaxial magnetism and FE polarization are intimately related to each other. At low temperature, Ca$_3$CoMnO$_6$ should undergo a JT distortion thereby losing uniaxial magnetism but should retain substantial magnetic anisotropy with orbital moment 0.56 $\mu_B$ along the chain direction. A strong electric polarization is predicted for the JT distorted Ca$_3$CoMnO$_6$ in the magnetic ground state with ↑↑↓↓ spin order not only along the c-axis but also perpendicular to the c-axis.

In Ca$_3$CoMO$_6$ (M = Co, Rh, Ir), the JT instability, uniaxial magnetism, spin arrangement, metal-metal interaction and SOC are intimately interrelated. The adjacent spins in each CoMO$_6$ chain of Ca$_3$CoMO$_6$ (M = Co, Rh, Ir) prefer the FM arrangement for M = Co and Rh, but the AFM arrangement for M = Ir. The magnetism of Ca$_3$CoMO$_6$ (M = Co, Rh, Ir) cannot be genuinely uniaxial because it undergoes a weak JT distortion. Nevertheless, the orbital moments of the TP Co$^{n+}$ ions, though strongly reduced by the distortion, are still substantial enough to produce strong easy-axis anisotropy along the chain direction. The d-state split pattern of the trigonal prism (TP) Co$^{n+}$ (n = 2, 3) ions that is consistent with the electronic and magnetic properties of Ca$_3$CoMO$_6$ (M = Co, Rh, Ir) is not given by (d$_2$, d$_{-2}$) < d$_0$ < (d$_1$, d$_1$), but by d$_0$ < (d$_2$, d$_{-2}$) < (d$_1$, d$_1$). The L = 2 configuration (d$_0$)$^4$(d$_2$, d$_{-2}$)$^3$(d$_1$, d$_1$)$^2$ of
the TP Co\(^{3+}\) ion in Ca\(_3\)Co\(_2\)O\(_6\) is a combined consequence of the FM spin arrangement between adjacent TP and OCT Co\(^{3+}\) ions, the direct metal-metal interaction between them mediated by their \(z^2\) orbitals, and the SOC of the TP Co\(^{3+}\) ion. In contrast to the case of Ca\(_3\)Co\(_2\)O\(_6\), the TP and OCT ions of Ca\(_3\)CoMO\(_6\) (M = Rh, Ir) have different oxidation states (+2 and +4, respectively), because the Co 3d orbital lies lower in energy, and is more contracted, than the Rh 4d and Ir 5d orbitals. The OCT M\(^{4+}\) ion has the \((1a)^1(1e)^4\) configuration for M = Rh but the \((1a)^2(1e)^3\) configuration for M = Ir. This difference reflects a combined consequence of the spin arrangement between adjacent TP Co\(^{2+}\) and OCT M\(^{4+}\) ions, the direct metal-metal interaction between them mediated by their \(z^2\) orbitals, and the SOC of the TP M\(^{4+}\) ions.

The spin exchanges of CuFeO\(_2\) are frustrated, as found for AgCrO\(_2\), but the two systems differ; the AFM inter-layer exchange \(J_4\) is strong in AgCrO\(_2\) but weak in CuFeO\(_2\), and the intra-layer exchange \(J_3\) is FM in AgCrO\(_2\) but AFM in CuFeO\(_2\). In contrast to the case of AgCrO\(_2\), therefore, the \(↑↑↓↓\) state is only slightly higher in energy than the helical spiral-spin state \(Q_{a+b}\) (q = 1/3) in CuFeO\(_2\) so that extrinsic factors such as oxygen vacancy and applied magnetic field can influence whether it adopts the \(↑↑↓↓\) or \(Q_{a+b}\) (q = 1/3) structure. The magnitudes of the FE polarization calculated for the model helical spiral-chain structures of CuFeO\(_2\) are in good agreement with experiment. The FE polarization of CuFeO\(_2\) arises largely from the asymmetric electron density distributions around the oxygen atoms, and the polarization direction is related to the associated dipole directions and to the handedness of the helical spin rotation. It is highly desirable to find a more general rule for predicting the
FE polarization of layered triangular antiferromagnets that are obtained by repeating a 1D chain possessing either helical or cycloidal spiral-spin order.

In YBaM₂O₅ (M = Mn, Fe, Co), the inter-slab M-O…O-M spin exchanges along the c-axis are strongly AFM. This together with the strong AFM intra-slab spin exchanges explains why the 3D AFM ordering in YBaM₂O₅ (M = Fe, Co) takes place at temperatures well above the room temperature (i.e., T_N = 430⁴ and 330 K,⁵ respectively) and why the ferrimagnetic ordering temperature of YBaMn₂O₅ is high (i.e., 167 K).² Our calculations show that the observed charge order patterns of YBaM₂O₅ (M = Mn, Fe, Co) are not determined by whether or not their transition-metal ions are JT-active.