Density Functional Theory Analysis of the Interplay between Jahn–Teller Instability, Uniaxial Magnetism, Spin Arrangement, Metal—Metal Interaction, and Spin—Orbit Coupling in Ca₃CoMO₆ (M = Co, Rh, Ir)

Yuemei Zhang,† Erjun Kan,† Hongjun Xiang,‡ Antoine Villesuzanne,§ and Myung-Hwan Whangbo*†

†Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204, United States, ‡Key Laboratory of Computational Physical Sciences (Ministry of Education) and Department of Physics, Fudan University, Shanghai 200433, P. R. China, and §CNRS, Université de Bordeaux, ICMCB, 87 Av. Dr. A. Schweitzer, 33608 Pessac cedex, France

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In the isostructural oxides Ca₃CoMO₆ (M = Co, Rh, Ir), the CoMO₆ chains made up of face-sharing CoO₆ trigonal prisms and MO₆ 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 Co⁵⁺ (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 Ca₃CoMo₆ (M = Co, Rh, Ir) are consistent with d₀ < (d₂, d₋₂) < (d₁, d₋₁) but not with (d₂, d₋₂) < d₀ < (d₁, d₋₁). The trigonal-prism Co⁵⁺ ion in Ca₃CoO₆ has the L = 2 configuration (d₀)²(d₂, d₋₂)⁵(d₁, d₋₁)⁵ because of the metal—metal interaction between adjacent Co⁵⁺ ions in each Co₂O₆ chain, which is mediated by their z² orbitals, and the spin—orbit coupling of the trigonal-prism Co⁵⁺ ion. The spins in each CoMO₆ chain of Ca₃CoMO₆ prefer the ferromagnetic arrangement for M = Co and Rh but the antiferromagnetic arrangement for M = Ir. The octahedral M⁴⁺ ion of Ca₃CoMo₆ has the (1a)²(1e)⁴ configuration for M = Rh but the (1a)³(1e)⁵ configuration for M = Ir, which arises from the difference in the spin—orbit coupling of the M⁴⁺ ions and the Co···M metal—metal interactions.

1. Introduction

For a magnetic system with transition-metal ions exhibiting uniaxial (i.e., Ising) magnetism, the ions have an unevenly filled degenerate d-state so that the ΔJc value of the lowest-lying Kramer’s doublet state is greater than 1.1 However, such a system has Jahn–Teller (JT) instability2 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.3 Indeed, uniaxial magnetism and JT instability were found to compete in the magnetic oxide Ca₃CoMnO₆,⁴

1. To whom correspondence should be addressed. E-mail: mike_whangbo@ncsu.edu.

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uniaxial, although it has strong magnetic anisotropy with the easy axis along the CoMnO₆ chain.

The magnetic oxides Ca₃CoM₆O₆ (M = Co, Rh, Ir) are uniaxial magnetic materials, so that the Co atoms of the TP CoO₆ exist as Co³⁺ ions at a trigonal prism site when the d-state split pattern is given by δ₀ < (d₂, d₋₂) < (d₁, d₋₁) in (a), (b), and (c), and by (d₃, d₋₃) < δ₀ < (d₁, d₋₁) in (d) and (e). That the TP Co atoms are present as high-spin ions, the CoM₆O₆ chains have uniaxial spins, and their intrachain spin arrangement is ferromagnetic (FM) for M = Co, Rh, and Ir, and hence, the M atoms of the MO₆ octahedra exist as M³⁺ ions at face-sharing trigonal prisms.

For Ca₃CoM₆O₆, the nearest-neighbor (NN) Co – M distance of the CoM₆O₆ 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 z² orbitals can be substantial. (Here the NN Co – Ir distance of 2.706 Å is taken from the structure of Ca₃CoIrO₆ optimized by DFT calculations. See below.) The X-ray photoemission study of Ca₃CoM₆O₆ revealed that the Co atoms of the TP CoO₆ exist as Co³⁺ ions for M = Co but as Co²⁺ ions for M = Rh and Ir, and hence, the M atoms of the MO₆ octahedra exist as M³⁺ ions for M = Co but as M⁴⁺ ions for M = Rh and Ir. The magnetic properties of Ca₃CoM₆O₆ (M = Co, Rh, Ir) show that the TP Co atoms are present as high-spin ions, the CoM₆O₆ chains have uniaxial spins, and their intrachain spin arrangement is ferromagnetic (FM) for M = Co and Rh, and Ir, and the same is presumed to be true for M = Ir. The electronic and magnetic properties of Ca₃CoM₆O₆ (M = Co, Rh, Ir) have been investigated in a number of DFT studies.17–25

It has been well established that the d-states of a transition metal ion at an isolated TP site with C₃ rotational symmetry are split as δ₀ < (d₂, d₋₂) < (d₁, d₋₁).26 This leads to L = 0 configuration (d₀)²(d₂, d₋₂)(d₁, d₋₁)² (Figure 3a) for an isolated TP high-spin Co³⁺ (d⁶) ion, hence predicting the absence of uniaxial magnetism. Thus, it was concluded that the TP Co³⁺ ion of Ca₃CoO₆ should have the L = 2 configuration (d₀)³(d₂, d₋₂)(d₁, d₋₁)² (Figure 3b) due to the interaction between the z² orbitals of adjacent TP and that the TP Co atoms are present as high-spin ions, the CoM₆O₆ chains have uniaxial spins, and their intrachain spin arrangement is ferromagnetic (FM) for M = Co, Rh, and Ir, and the same is presumed to be true for M = Ir. The electronic and magnetic properties of Ca₃CoM₆O₆ (M = Co, Rh, Ir) have been investigated in a number of DFT studies.17–25

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OCT $\text{Co}^{3+}$ ions. In the DFT study of $\text{Ca}_3\text{Co}_2\text{O}_6$ by Wu et al., 21 spin–orbit coupling (SOC) interactions were found essential for the occurrence of the L = 2 configuration $(d_0)^1(d_1, d_{-1})^2$: the TP $\text{Co}^{3+}$ ion has the $(d_0)^1(d_2, d_{-2})^2(d_1, d_{-1})^2$ configuration if SOC interactions are included, but the $(d_0)^1(d_2, d_{-2})^2(d_1, d_{-1})$ configuration otherwise. Nevertheless, they assumed the split pattern of the TP $\text{Co}^{3+}$ ion to be $(d_2, d_{-2}) < (d_1, d_{-1})$, which leads to the L = 2 configuration $(d_2, d_{-2})^2(d_0)^1(d_1, d_{-1})^2$ (Figure 3c) even if the SOC effect is not included. Furthermore, Burnus et al. 27 employed this L = 2 configuration for the TP $\text{Co}^{3+}$ ion to interpret their X-ray absorption and X-ray magnetic dichroism data of $\text{Ca}_3\text{Co}_2\text{O}_6$, and concluded that the $d_0 < (d_2, d_{-2}) < (d_1, d_{-1})$ pattern is incorrect for the TP $\text{Co}^{3+}$ 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 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 $\text{Co}^{3+}$ ion, being aligned along the C2 axis of the TP $\text{CoO}_6$ layer, 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 (Figure 2a) regardless of whether the TP ion is $\text{Co}^{3+}$ or $\text{Co}^{2+}$, 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 $\text{Ca}_3\text{CoRhO}_6$ because it gives rise to the L = 0 configuration $(d_0)^2(d_2, d_{-2})^2(d_1, d_{-1})^2$ for the TP $\text{Co}^{3+}$ (d$^4$) ion (Figure 3d). In contrast, the $d_0 < (d_2, d_{-2}) < (d_1, d_{-1})$ split pattern gives the L = 2 configuration $(d_2, d_{-2})^2(d_0)^1(d_1, d_{-1})^2$ (Figure 3c), and the latter is consistent with the density functional calculations for $\text{Ca}_3\text{CoRhO}_6$ by Wu et al. 25 In interpreting their X-ray absorption and X-ray magnetic dichroism data of $\text{Ca}_3\text{CoRhO}_6$, Burnus et al. 27 used the $d_0 < (d_2, d_{-2}) < (d_1, d_{-1})$ pattern for the TP $\text{Co}^{3+}$ 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 Co$\text{O}_6$ chains in $\text{Ca}_3\text{Co}_2\text{O}_6$ have the FM arrangement as found in $\text{Ca}_3\text{Co}_2\text{O}_6$ and $\text{Ca}_3\text{CoRhO}_6$. (b) In all three oxides $\text{Ca}_3\text{Co}_2\text{O}_6$ (M = Co, Rh, Ir), the OCT $\text{M}^{4+}$ chains of $\text{Ca}_3\text{Co}_2\text{O}_6$ have the C2 rotational symmetry in the high-$\mu$$_{\text{L}}$ structure, but do not in the low-$\mu$$_{\text{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$$_{\text{L}}$ structure. In discussing the spin and orbital moments of the TP and OCT ions of $\text{Ca}_3\text{Co}_2\text{O}_6$ (M = 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 $\text{Ca}_3\text{Co}_2\text{O}_6$ and $\text{Ca}_3\text{CoRhO}_6$ by optimizing the atomic positions of $\text{Ca}_3\text{CoIrO}_6$ by Burnus et al. 29

2. Calculations

To optimize the crystal structures of $\text{Ca}_3\text{Co}_2\text{O}_6$ (M = Co, Rh, Ir) in the presence and absence of C2 rotational symmetry, we employed the projector augmented wave (PAW) method encoded in the Vienna ab initio simulation package (VASP) 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. 31 In addition, SOC effects 32 were considered by performing LSDA + U + SOC calculations with the spins oriented parallel and perpendicular to the Co$\text{O}_6$ chain direction (hereafter the |c- and ±c-spin orientations, respectively). The convergence threshold for our LSDA + U + SOC calculations was set to $10^{-5}$ eV in energy and $10^{-2}$ eVÅ in force with the plane-wave cutoff energy of 400 eV and a set of 3 × 3 × 3 k-points for the irreducible Brillouin zone. For $\text{Ca}_3\text{CoIrO}_6$, only the cell parameters have been reported. 33 Therefore, we determined the atomic positions of $\text{Ca}_3\text{CoRhO}_6$ by optimizing the crystal structure on the basis of LSDA + U + SOC calculations. This optimization leads to two kinds of structures for each $\text{Ca}_3\text{Co}_2\text{O}_6$ (M = Co, Rh, Ir), namely, one with high orbital moment ($\mu$$_{\text{L}}$) and the other with low-$\mu$$_{\text{L}}$. For the TP Co$^{3+}$ ($n = 2, 3$), ions. As found for $\text{Ca}_3\text{CoMnO}_6$, 4 the Co$\text{O}_6$ chains of $\text{Ca}_3\text{Co}_2\text{O}_6$ have the C2 rotational symmetry in the high-$\mu$$_{\text{L}}$ structure, but do not in the low-$\mu$$_{\text{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$$_{\text{L}}$ structure. In discussing the spin and orbital moments of the TP and OCT ions of $\text{Ca}_3\text{Co}_2\text{O}_6$ (M = Co, Rh, Ir) as well as their density of states (DOS), we have carried out LSDA + U + SOC calculations for the experimental and the optimized structures of $\text{Ca}_3\text{Co}_2\text{O}_6$ and $\text{Ca}_3\text{CoRhO}_6$ and for the optimized structure of $\text{Ca}_3\text{CoIrO}_6$ by using the full-potential linearized augmented plane wave (FLAPW) method 34 encoded in the WIEN2k package. 35 5 × 5 × 5 k-points for the irreducible Brillouin zone, the threshold of 10$^{-5}$ Ry for the energy convergence, the cutoff energy parameters of $\mathbf{R}_{\text{K}}$$_{\text{max}}$ = 7 and $\mathbf{G}_{\text{max}}$ = 12, and the energy threshold of −9.0 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 geometry optimization with the LSDA + U + SOC (VASP), calculations.
we used $U_{\text{eff}} = 4 \text{ eV}$ on Co for Ca$_3$Co$_2$O$_6$, $U_{\text{eff}} = 4 \text{ eV}$ on Co, and $U_{\text{eff}} = 2 \text{ eV}$ for Rh and Ir for Ca$_3$CoMO$_6$ (M = Rh, Ir). (We note that, for LSDA+U and LSDA+U+SOC calculations, only the difference $U - U_{\text{eff}}$ matters for the calculations.) These parameters are quite similar to those employed by Wu et al. in their DFT studies of Ca$_3$Co$_2$O$_6$ and Ca$_3$CoRhO$_6$. We also employed these parameters for our LSDA+U and LSDA+U+SOC (WIEN2k) calculations on Ca$_3$CoMO$_6$ (M = Co, Rh, Ir) to find that the use of $U_{\text{eff}} = 4$ and 2 eV on Co and M, respectively, does not lead to magnetic insulating states for Ca$_3$CoMO$_6$ (M = Rh, Ir) but the use of $U_{\text{eff}} = 4$ eV on both Co and M does. Hereafter, the $U_{\text{eff}}$ values on Co, Rh, and Ir will be designated as $U_{\text{eff}}($Co), $U_{\text{eff}}($Rh), and $U_{\text{eff}}($Ir), respectively.

Possible ordered spin arrangements for each CoMO$_6$ chain of Ca$_3$CoMO$_6$ (M = Co, Rh, Ir) include the FM (i.e., $\uparrow\uparrow\uparrow\uparrow$), antiferromagnetic (AFM) (i.e., $\uparrow\downarrow\downarrow\downarrow$), and $\uparrow\uparrow\downarrow\downarrow$ arrangements. It should be noted that the AFM state represents a ferromagnetic 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 Ca$_3$CoMO$_6$ (M = Co, Rh, Ir)

Our WIEN2k calculations show that, for Ca$_3$Co$_2$O$_6$, 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 is necessary to obtain the $L = 2$ configuration $(d_{\uparrow\uparrow})^2(d_{\downarrow\downarrow})^2(d_{\downarrow\uparrow})^2(d_{\uparrow\downarrow})^2$ for the TP Co$^{3+}$ ion, as found by Wu et al. For both Ca$_3$CoRhO$_6$ and Ca$_3$CoIrO$_6$, 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 Ca$_3$Co$_2$O$_6$, while both the FM and the opposite directions otherwise. 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.

### 4. Jahn–Teller Distortion and Magnetic Anisotropy

To see whether Ca$_3$CoMO$_6$ (M = Co, Rh, and Ir) undergoes a JT distortion, all the structures of Ca$_3$CoMO$_6$ (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 C$_3$ rotational symmetry for each CoMO$_6$ chain. The atom positions of the optimized structures of Ca$_3$CoMO$_6$ (M = Co, Rh, Ir) are summarized in Tables S1–S3 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 1, and the spin and orbital moments ($\mu_S$ and $\mu_L$).

### Table 1. Relative Energies $\Delta E$ (meV/Structures) 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

| Structure                  | Co$_3$CoO$_6$ | Ca$_3$CoRhO$_6$ | Ca$_3$CoIrO$_6$ |
|----------------------------|---------------|-----------------|-----------------|
| experimental with C$_3$ axis | 94.3          | 65.7            |                 |
| optimized with C$_3$ axis   | 65.5          | 35.2            | 139.8           |
| optimized with no C$_3$ axis| 0.0           | 0.0             | 0.0             |

*For each Ca$_3$CoMO$_6$ (M = Co, Rh, Ir), the optimization was carried out for the FM state.

### Table 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$_3$CoMO$_6$ Obtained from the LSDA+U+SOC (WIEN2k) Calculations with $U_{\text{eff}}($Co) = 4 eV

| Structure                  | Co$^{3+}$ (TP) | Co$^{3+}$ (OCT) |
|----------------------------|----------------|-----------------|
| geometry used              |                |                 |
| experiment with C$_3$ axis | 2.94           | 1.58            |
| optimized with C$_3$ axis  | 2.94/2.94      | 1.48/1.48       |
| optimized with no C$_3$ axis| 2.92/2.39      | 0.31/0.45       |

*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.

The orbital and spin moment arrangements have the same direction when they have the same sign, and the opposite directions otherwise.

### Table 3. Spin and Orbital Moments ($\mu_S$ and $\mu_L$, Respectively) of the TP and OCT Co$^{3+}$ and OCT Rh$^{3+}$ Ions in the FM State of Ca$_3$CoRO$_6$ Obtained from the LSDA+U+SOC (WIEN2k) Calculations with $U_{\text{eff}}($Co) = $U_{\text{eff}}($Rh) = 4 eV

| Structure                  | Co$^{3+}$ (TP) | Co$^{3+}$ (OCT) | Rh$^{3+}$ (OCT) |
|----------------------------|----------------|-----------------|-----------------|
| geometry used              |                |                 |                 |
| experiment with C$_3$ axis | 2.71           | 1.76            | 0.49            |
| optimized with C$_3$ axis  | 2.69/2.69      | 1.76/1.76       | 0.59/0.59       |
| optimized with no C$_3$ axis| 2.64/2.64      | 0.50/0.50       | 0.31/0.31       |

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

### Table 4. Spin and Orbital Moments ($\mu_S$ and $\mu_L$, Respectively) of the TP Co$^{3+}$ and OCT Ir$^{3+}$ Ions in the FM State of Ca$_3$CoO$_6$ Obtained from the LSDA+U+SOC (WIEN2k) Calculations with $U_{\text{eff}}($Co) = $U_{\text{eff}}($Ir) = 4 eV

| Structure                  | Co$^{3+}$ (TP) | Ir$^{3+}$ (OCT) |
|----------------------------|----------------|-----------------|
| geometry used              |                |                 |
| optimized with C$_3$ axis  | 2.62/2.62      | 1.77/1.77       |
| optimized with no C$_3$ axis| 2.62/2.62      | 0.72/0.44       |

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

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.
The largest atom displacement is 0.044 Å in Ca₃Co₂O₆, 0.064 Å in distortions in the magnetic ground state of (a) Ca₃Co₂O₆, (b) Ca₃CoRhO₆, and (c) Ca₃CoIrO₆ with respect to their positions of the experimental structures for Ca₃CoO₆ and Ca₃CoRhO₆ and with respect to their positions of the optimized structure with C₃ symmetry for Ca₃CoIrO₆. The largest atom displacement is 0.044 Å in Ca₃CoO₆, 0.064 Å in Ca₃CoRhO₆, and 0.051 Å in Ca₃CoIrO₆. In each panel, the left side shows a perspective view of the atom displacements in the CoO₆ trigonal prisms and MO₆ octahedra.

or Ir), the optimized structure without C₃ symmetry is more stable than that with C₃ symmetry (i.e., ΔE = 65.5, 35.2, and 139.8 meV/FU for M = Co, Rh, and Ir, respectively). This shows that the structural change of Ca₃CoMO₆ (M = Co, Rh or Ir), from the structure with C₃ symmetry to that without C₃ symmetry, is a JT distortion. Figure 4 shows the atom displacements involved in the JT distortions of Ca₃CoMO₆ (M = Co, Rh, Ir), with respect to the experimental structure for M = Co and Rh, and with respect to the optimized structure with C₃-rotational symmetry for M = Ir. In Ca₃Co₂O₆ with TP Co³⁺ 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 Ca₃CoRhO₆ and Ca₃CoIrO₆ with TP Co³⁺ 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 Co³⁺ ions are reduced by the JT distortion but the JT distortions are not strong enough to completely quench the orbital angular moment of Co³⁺ (Tables 2–4). As found for Ca₃CoMnO₆, the oxides Ca₃CoMO₆ (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 Ca₃Co₂O₆, Ca₃CoRhO₆, and Ca₃CoIrO₆ 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 Ca₃Co₂O₆, Ca₃CoRhO₆, and Ca₃CoIrO₆, respectively, which represent very strong easy-axis anisotropy. This renders the observed anisotropic magnetic character to Ca₃Co₂O₆, Ca₃CoRhO₆, and Ca₃CoIrO₆.

5. One-Electron Picture in DFT+U Description: Analysis of the Electronic Structure of Ca₃Co₂O₆

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.

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and OCT Co$^{3+}$ ions is transferred to the (d$_2$, d$_{-2}$) 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 Figure 7a, where the z$^2$ and z$^4$ 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$^2$ and z$^4$ levels should be nearly the same. The highest occupied level resulting from the z$^2$ orbitals of the two Co$^{3+}$ ions is the σ* level, in which the weight of the TP z$^2$ orbital is larger than the OCT z$^2$ orbital because the former lies higher in energy than the latter. In the DFT+U level of description, the occupied σ* level lies below the empty (d$_2$, d$_{-2}$) level of the TP Co$^{3+}$ ion. The effect of the SOC interaction at the TP Co$^{3+}$ ion site is depicted in Figure 8a, where the SOC splits the unoccupied degenerate level (d$_2$, d$_{-2}$) into the d$_2$-below-d$_{-2}$ pattern since $\lambda$ < 0 for Co$^{3+}$ (d$^6$). When the unoccupied d$_2$ level is lowered below the occupied σ* level, an electron transfer occurs from the σ* level to the d$_2$ level. Since the σ* level has a greater weight on the TP z$^2$ 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$_{-2}$)$^2$ to the L = 2 configuration (d$_0$)$^2$(d$_2$, d$_{-2}$)$^2$(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$_0$)$^2$(d$_2$, d$_{-2}$)$^2$(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 (Figure 8b), the TP Co$^{3+}$ ion would have the (d$_0$)$^2$(d$_2$, d$_{-2}$)$^2$(d$_1$, d$_{-1}$)$^2$ configuration in both DFT+U and DFT+U+SOC levels of descriptions because the σ* level remains unoccupied regardless of whether or not the singly occupied (d$_2$, d$_{-2}$) level is split by the effect of SOC.
6. Electronic Structures of Ca₃CoMO₆ (M = Rh, Ir)

The reason why Ca₃CoMoO₆ (M = Rh, Ir) has Co²⁺ and M⁴⁺ ions in the TP and OCT sites is that the Co 3d orbitals lie 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 Co²⁺ and OCT Rh⁴⁺ ions, which give rise to the configuration (z²)(x²−y², xy)³(xz, yz)² for the TP Co²⁺ ion and the configuration (1a)¹(1e)³ for the OCT Rh⁴⁺ ion, can be understood in terms of the orbital interaction diagrams shown in Figure 9a. Here the two adjacent ions have the FM arrangement, and the midpoint between the z² and x²−y² orbitals is placed higher in energy for the M⁴⁺ (M = Rh, Ir) ion than that for the Co²⁺ ion, because the Rh 4d and Ir 5d orbital is more diffuse, and lies higher in energy, than the Co 3d orbital. The σ¹ orbitals lie higher in energy in the FM than in the AFM spin arrangement.

As shown by the projected DOS plots for the FM state of Ca₃CoRhO₆ in Figure 10, the LSDA+U+SOC (WIEN2k) calculations with U_eff(Co) = 4 eV predict Ca₃CoRhO₆ to be a magnetic insulator, whereas our LSDA+U calculations with U_eff(Co) = 4 eV predict Ca₃CoRhO₆ to be a metal (see Figure S1 of the Supporting Information). The LSDA+U and LSDA+U+SOC calculations with U_eff(Co) = 4 eV and U_eff(Rh) = 2 eV both predict Ca₃CoRhO₆ to be a metal, see Figure S2 of the Supporting Information. The projected DOS plots from the LSDA+U+SOC calculations show that the local electronic structure of the TP Co²⁺ ion is given by (z²)(x²−y², xy)³(xz, yz)² and that of the OCT Rh⁴⁺ ion by (1a)¹(1e)³. This explains the uniaxial magnetism of Ca₃CoRhO₆ brought about by the L = 2 configuration of the TP Co²⁺ ion and why the orbital moment µₐ of the OCT Rh⁴⁺ ion is nearly zero (see Table 3) in the LSDA+U+SOC calculations.

The above discussion for the FM state of Ca₃CoRhO₆, which accounts for the configuration (z²)(x²−y², xy)³(xz, yz)² for the TP Co²⁺ ion and the configuration (1a)¹(1e)³ for the OCT Rh⁴⁺ ion, is also applicable to the FM state of Ca₃CoIrO₆. The AFM spin arrangement (i.e., the ferrimagnetic state) of Ca₃CoIrO₆ has a slightly different picture for the local electronic structure of the OCT Ir⁴⁺ ion. The projected DOS plots for the FM state of Ca₃CoIrO₆, which accounts for the configuration (z²)(x²−y², xy)³(xz, yz)² for the TP Co²⁺ ion and the configuration (1a)¹(1e)³ for the OCT Rh⁴⁺ ion, is not described by d₅ ion, because the Rh 4d and Ir 5d orbitals are a heavier element than Co. Therefore, the local electronic structure of M⁴⁺ (d⁵) ion can be more strongly affected by the SOC compared with that of the OCT Co³⁺ (d⁶) ion in Ca₃CoMoO₆. In principle, the (2s)² configuration can be approximated by either (1a)¹(1e)³ or (1a)¹(1e)³ (see Figure 2b). The angular momentum behavior of the 1a (i.e., z²) orbital is described by d₅ and those of the 1e orbitals by linear combinations of d₁± and d₂±, namely, by (2/3)(1−)−½x²−½yz and (2/3)(1−)−½xy−½xz. Thus, the orbital moment µₐ of the OCT M⁴⁺ (d⁵) ion would be negligible if its electron configuration is close to (1a)³(1e)⁴. However, this would not be the case if the electron configuration is close to (1a)³(1e)⁴. As discussed below, it depends on the spin arrangement between adjacent Co²⁺ and M⁴⁺ ions, the direct metal–metal interaction between them, and the SOC of the M⁴⁺ ion whether the local electronic structure of the OCT M⁴⁺ (d⁵) ion is close to (1a)³(1e)⁴ or to (1a)³(1e)³.

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the overlap between them is good hence raising the $\sigma^d$ level.

In the LSDA+U+SOC calculations, both the $\sigma^d$ and $\sigma^4$ levels are both occupied. In contrast, the $\sigma^d$ level is filled but the $\sigma^4$ level is not. Consequently, the Co$\cdots$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$\cdots$M metal–metal interaction in Ca$_3$CoMO$_6$ (M = Rh, Ir) should be weak because the TP Co$^{3+}$ ion has a large displacement in the JT distorted structure. The NN Co$\cdots$Rh and Co$\cdots$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$\cdots$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$^{3+}$ 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$^{3+}$ ion is large in the JT distorted structures of Ca$_3$CoMO$_6$ (M = Rh, Ir).

The differences in the $z^\perp$ 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 $z^\perp$ orbitals is the $\sigma^d$ level, which decreases in energy with lengthening the NN Co$\cdots$M distance and with increasing the difference in the contractedness of the Co and M $z^\perp$ orbitals. Thus, it is understandable that the two $z^\perp$ orbitals of adjacent TP and OCT ions have four electrons in Ca$_3$CoIrO$_6$ (i.e., the $\sigma^4$ level is occupied) but three electrons in Ca$_3$Co$_2$O$_6$ and Ca$_3$CoRhO$_6$ (i.e., the $\sigma^4$ level is unoccupied). The latter is equivalent to a singly occupied $z^\perp$ orbital at the TP Co$^{3+}$ ion in Ca$_3$Co$_2$O$_6$, but that at the OCT Rh$^{4+}$ ion in Ca$_3$Co$_2$O$_6$, due to the unequal weights of the TP and OCT $z^\perp$ orbitals in the $\sigma^4$ level (Figure 7 vs Figure 9). A higher-lying $\sigma^4$ level and a lower-lying $\sigma^d$ level are obtained when adjacent TP and OCT ions have an FM spin arrangement rather than an AFM spin arrangement. Thus, the FM arrangement is energetically more favorable when the $\sigma^d$ 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 $\sigma^4$ 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$^{3+}$ 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$^{3+}$ ($n = 2, 3$) 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$_1$, d$_{-1}$) but (d$_2$, d$_{-2}$) < (d$_1$, d$_{-1}$). The $L = 2$ configuration (d$_0$)(d$_2$, d$_{-2}$)(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$^2$ 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.

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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.