X-ray absorption and x-ray magnetic dichroism study on Ca$_3$CoRhO$_6$ and Ca$_3$FeRhO$_6$

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Using x-ray absorption spectroscopy at the Rh-$L_{2,3}$, Co-$L_{2,3}$, and Fe-$L_{2,3}$ edges, we find a valence state of Co$^{2+}$/Rh$^{4+}$ in Ca$_3$CoRhO$_6$ and of Fe$^{3+}$/Rh$^{3+}$ in Ca$_3$FeRhO$_6$. X-ray magnetic circular dichroism spectroscopy at the Co-$L_{2,3}$ edge of Ca$_3$CoRhO$_6$ reveals a giant orbital moment of about 1.7$\mu_B$, which can be attributed to the occupation of the minority-spin $d_{xy}$ orbital state of the high-spin Co$^{2+}$ ($3d^7$) ions in trigonal prismatic coordination. This active role of the spin-orbit coupling explains the strong magnetocrystalline anisotropy and Ising-like magnetism of Ca$_3$CoRhO$_6$.

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I. INTRODUCTION

The quasi one-dimensional transition-metal oxides Ca$_3$ABO$_6$ ($A$ = Fe, Co, Ni, ...; $B$ = Co, Rh, Ir, ...) have attracted a lot of interest in recent years because of their unique electronic and magnetic properties. The structure of Ca$_3$ABO$_6$ contains one-dimensional (1D) chains consisting of alternating face-sharing AO$_6$ trigonal prisms and BO$_6$ octahedra. Each chain is surrounded by six parallel neighboring chains forming a triangular lattice in the basal plane. Peculiar magnetic and electronic behaviors are expected to be related to geometric frustration in such a triangle lattice with antiferromagnetic (AFM) interchain interaction and Ising-like ferromagnetic (FM) intrachain coupling. Ca$_3$CoO$_2$O$_6$, which realizes such a situation, shows stair-step jumps in the magnetization at regular intervals of the applied magnetic field of $M_s/3$, suggesting ferrimagnetic spin alignment. It has a saturation magnetization of $M_s = 4.8\mu_B$ per formula unit at around 4 T. Studies on the temperature and magnetic-field dependence of the characteristic spin-relaxation time suggest quantum tunneling of the magnetization similar to single-molecular magnets. An applied magnetic field induces a large negative magnetoresistance, apparently not related to the three-dimensional magnetic ordering. Band-structure calculations using the local-spin-density approximation plus Hubbard U (LSDA+U) predicted that the Co$^{3+}$ ion at the trigonal site, being in the high-spin (HS) state ($S = 2$), has a giant orbital moment of 1.57$\mu_B$ due to the occupation of minority-spin $d_2$ orbital, while the Co$^{3+}$ ion at the octahedral site is in the low-spin (LS) state ($S = 0$). An x-ray absorption and magnetic circular dichroism study at the Co-$L_{2,3}$ edge has confirmed this prediction. The Ising nature of the magnetism of Ca$_3$CoO$_2$O$_6$.

Ca$_3$CoRhO$_6$ and Ca$_3$FeRhO$_6$ have the same crystal structure as Ca$_3$Co$_2$O$_6$, but different magnetic and electronic properties: Neutron diffraction and magnetization measurements also indicated intrachain-FM and interchain-AFM interactions in Ca$_3$CoRhO$_6$ like in Ca$_3$Co$_2$O$_6$. In contrast, susceptibility data on Ca$_3$FeRhO$_6$ reveal a single transition into a three-dimensional AFM. Although Ca$_3$CoRhO$_6$ has a similar magnetic structure as Ca$_3$Co$_2$O$_6$, it exhibits considerable differences in the characteristic temperatures in the magnetic susceptibility. The high-temperature limit of the magnetic susceptibility shows a Curie-Weiss behavior with a positive Weiss temperature of 150 K for Ca$_3$CoRhO$_6$, while 30 K was found for Ca$_3$Co$_2$O$_6$. The measured magnetic susceptibility undergoes two transitions at $T_c_1 = 90$ K and $T_c_2 = 25$ K for Ca$_3$CoRhO$_6$, and at $T_c_3 = 24$ K and $T_c_4 = 12$ K for Ca$_3$Co$_2$O$_6$, which were attributed to FM-intrachain and AFM-interchain coupling, respectively. In contrast, Ca$_3$FeRhO$_6$ has an AFM ordering below $T_N = 12$ K. Unlike Ca$_3$Co$_2$O$_6$, there is only one plateau at 4 T and no saturation even at 18 T in the magnetization of Ca$_3$CoRhO$_6$ at 70 K. A partially disordered state in Ca$_3$CoRhO$_6$ has been inferred by the previous work of Niitaka et al.

In order to understand the contrasting magnetic properties of Ca$_3$CoRhO$_6$ and Ca$_3$FeRhO$_6$, and, particularly, the type and origin of the intrachain magnetic coupling of these quasi 1D systems, the valence, spin, and orbital states have to be clarified. However, these issues have been contradictoriy discussed in previous theoretical and experimental studies. The general-gradient-approximated (GGA) density-functional band calculations suggest a Co$^{3+}$/Rh$^{3+}$ state in Ca$_3$CoRhO$_6$, while LSDA+U calculations with inclusion of the spin-orbit coupling favor a Co$^{2+}$/Rh$^{4+}$
state and, again, a giant orbital moment due to the occupation of minority-spin $d_0$ and $d_2$ orbitals. Neutron diffraction experiments on Ca$_3$CoRhO$_6$$^{8,22}$ suggest the Co$^{3+}$/Rh$^{3+}$ state. However, based on the magnetic susceptibility$^5$ and x-ray photoemission spectroscopy$^{23}$ the Co$^{2+}$/Rh$^{4+}$ state was proposed. For Ca$_3$FeRhO$_6$, the Fe$^{2+}$/Rh$^{3+}$ state was suggested in a magnetic susceptibility study,$^3$ whereas Mössbauer spectroscopy indicates a Fe$^{3+}$ state,$^{19}$ and thus Rh$^{3+}$.

In order to settle the above issues, in this work we first clarify the valence state of the Rh, Co, and Fe ions in Ca$_3$CoRhO$_6$ and Ca$_3$FeRhO$_6$ using x-ray absorption spectroscopy (XAS) at the $L_{2,3}$ edges of Rh, Co, and Fe. We reveal a valence state of Co$^{2+}$/Rh$^{4+}$ in Ca$_3$CoRhO$_6$ and of Fe$^{3+}$/Rh$^{3+}$ in Ca$_3$FeRhO$_6$. Then, we investigate the orbital occupation and magnetic properties using x-ray magnetic circular dichroism (XMCD) experiments at the Co-$L_{2,3}$ edge of Ca$_3$CrRhO$_6$. We find a minority-spin $d_{0t2}$ occupation for the HS Co$^{2+}$/Rh$^{3+}$ ground state and, thus, a giant orbital moment of about 1.7$\mu_B$. As will be seen below, our results account well for the previous experiments.

II. EXPERIMENTAL

Polycrystalline samples were synthesized by a solid-state reaction and characterized by x-ray diffraction to be single phase.$^5$ The Rh-$L_{2,3}$ XAS spectra were measured at the NSRRC 15B beamline in Taiwan, which is equipped with a double-Si(111) crystal monochromator for photon energies above 2 keV. The photon-energy resolution at the Rh-$L_{2,3}$ edge ($h\nu \approx 3000$–3150 eV) was set to 0.6 eV. The Fe-$L_{2,3}$ XAS spectrum of Ca$_3$FeRhO$_6$ was measured at the NSRRC Dragon beamline with a photon-energy resolution of 0.25 eV. The main peak at 709 eV of the Fe-$L_{3}$ edge of single-crystalline Fe$_2$O$_3$ was used for energy calibration. The Co-$L_{2,3}$ XAS and XMCD spectra of Ca$_3$CoRhO$_6$ were recorded at the ID8 beamline of ESRF in Grenoble with a photon-energy resolution of 0.2 eV. The sharp peak at 777.8 eV of the Co-$L_3$ edge of single-crystalline CoO was used for energy calibration. The Co-$L_{2,3}$ XMCD spectra were recorded in a magnetic field of 5.5 T; the photons were close to fully circularly polarized. The sample pellets were cleaved in situ in order to obtain a clean surface. The pressure was below $5 \times 10^{-10}$ mbar during the measurements. All data were recorded in total-electron-yield mode.

III. XAS AND VALENCE STATE

We first concentrate on the valence of the rhodium ions in both studied compounds. For 4$d$ transition-metal oxides, the XAS spectrum at the $L_{2,3}$ edge reflects basically the unoccupied $t_{2g}$- and $e_g$-related peaks in the $O_h$ symmetry. This is due to the larger band-like character and the stronger crystal-field interaction of the 4$d$ states as well as due to the weaker intra-atomic interactions as compared with 3$d$ transition-metal oxides, where intra-atomic multiplet interactions are dominant. The intra-atomic multiplet and spin-orbit interactions in 4$d$ elements only modify the relative intensity of the $t_{2g}$- and $e_g$-related peaks. Fig. 1 shows the XAS spectra at the Rh-$L_{2,3}$ edges of Ca$_3$FeRhO$_6$ (dashed line) and Ca$_3$CoRhO$_6$ (solid line). The Rh-$L_{2,3}$ spectrum shows a simple, single-peaked structure at both Rh-$L_2$ and Rh-$L_3$ edges for Ca$_3$FeRhO$_6$, while an additional low-energy shoulder is observed for Ca$_3$CoRhO$_6$. Furthermore, the peak in the Ca$_3$CoRhO$_6$ spectrum is shifted by 0.8 eV to higher energies compared to that of the Ca$_3$FeRhO$_6$.

The single-peaked spectral structure for Ca$_3$FeRhO$_6$ indicates Rh$^{3+}$ (4$d^6$) with completely filled $t_{2g}$ orbitals, i.e. only transitions from the 2$p$ core levels to the $e_g$ states are possible. The results are in agreement with Mössbauer spectroscopy.$^{19}$ The shift to higher energies from Ca$_3$FeRhO$_6$ to Ca$_3$CoRhO$_6$ reflects the increase in the Rh valence from Rh$^{3+}$ to Rh$^{4+}$ as we can learn from previous studies on 4$d$ transition-metal compounds.$^{24,25,26,27}$ Furthermore, for Ca$_3$CoRhO$_6$ the spectrum shows a weak low-energy shoulder, which is weaker at the Rh-$L_2$ edge than at the Rh-$L_3$ edge. This shoulder can be attributed to transitions from the 2$p$ core levels to the $t_{2g}$ state, reflecting a 4$d^5$ configuration with one hole at the $t_{2g}$ state. Such spectral features were found earlier for Ru$^{3+}$ in Ru(NH$_3$)$_5$Cl$_6$.$^{24,28}$ Detailed calculations reveal that the multiplet and spin-orbit interactions suppress the $t_{2g}$-related peak at the $L_2$ edge for a 4$d^5$ configuration.$^{24,25,26,27}$ Thus, we find a Rh$^{4+}$ (4$d^5$) state for Ca$_3$CoRhO$_6$. Having determined a Rh$^{3+}$ state in Ca$_3$FeRhO$_6$ and a Rh$^{4+}$ state in Ca$_3$CoRhO$_6$, we turn to the Fe-$L_{2,3}$ and the Co-$L_{2,3}$ XAS spectra to further confirm the Fe$^{3+}$ state and the Co$^{2+}$ state, as expected for charge balance.

FIG. 1: The Rh-$L_{2,3}$ XAS spectra of Ca$_3$CoRhO$_6$ and Ca$_3$FeRhO$_6$ and a schematic energy level diagram for Rh$^{3+}$ 4$d^5$ and Rh$^{4+}$ 4$d^4$ configurations in octahedral symmetry.
The main peak of the Fe\textsuperscript{2+} XAS spectrum of Ca\textsubscript{3}FeRhO\textsubscript{6} in Fig. 2(g) can be well reproduced with this trigonal crystal field of 0.9 eV and in addition a mixing parameter \(V_{\text{mix}} = 0.4\) eV, which mixes the \(d_{z^2}\) with the \(d_{x^2-y^2}\) orbitals. The result for this Fe with the \(3d^5\) high-spin configuration is presented in curve (f).

We note that curve (f) has been generated with the Fe in the trivalent state. As a check, we have also tried to fit the experimental spectrum of Ca\textsubscript{3}FeRhO\textsubscript{6} using a divalent Fe ansatz. However, the simulation does not match, as is illustrated in curve (h), in which we have used the same trigonal crystal field splitting of 0.9 eV and mixing parameter of 0.4 eV. To conclude, the Fe-L\textsubscript{2,3} and Rh-L\textsubscript{2,3} XAS spectra of Ca\textsubscript{3}FeRhO\textsubscript{6} firmly establish the Fe\textsuperscript{3+}/Rh\textsuperscript{4+} scenario.

For the Ca\textsubscript{3}CoRhO\textsubscript{6} system, the Rh-L\textsubscript{2,3} XAS spectra suggest that the Rh ions are tetravalent, implying that the Co ions should be divalent. To confirm this Co\textsuperscript{2+}/Rh\textsuperscript{4+} scenario we have to study explicitly the valence of the Co ion. Fig. 3 shows the Co-L\textsubscript{2,3} XAS spectra of Ca\textsubscript{3}CoRhO\textsubscript{6} together with CoO as a Co\textsuperscript{2+} and Ca\textsubscript{3}Co\textsubscript{2}O\textsubscript{6} as a Co\textsuperscript{3+} reference.\textsuperscript{17} Again we see a shift to higher energies from CoO to Ca\textsubscript{3}Co\textsubscript{2}O\textsubscript{6} by about one eV. The Ca\textsubscript{3}CoRhO\textsubscript{6} spectrum lies at the same energy position as the CoO spectrum confirming the Co\textsuperscript{2+}/Rh\textsuperscript{4+} scenario\textsuperscript{21} and ruling out the Co\textsuperscript{3+}/Rh\textsuperscript{3+} scenario.\textsuperscript{20} The result is fully consistent with the above finding from the Rh-L\textsubscript{2,3} edge of Ca\textsubscript{3}CoRhO\textsubscript{6} and in agreement with previous results from x-ray photoemission spectroscopy.\textsuperscript{23}

**IV. XMCD AND ORBITAL OCCUPATION/MOMENT**

After determining the valence states of Rh, Fe, and Co ions we turn our attention to the orbital occupation and magnetic properties of the Co\textsuperscript{2+} ion at the trigonal prism site. This is motivated by the consideration that Co\textsuperscript{2+} ions may have a large orbital moment,\textsuperscript{36} whose size depends on details of the crystal field, while the high-spin Fe\textsuperscript{3+} (\(3d^5\)) and low-spin Rh\textsuperscript{3+} (\(4d^8\)) ions in Ca\textsubscript{3}FeRhO\textsubscript{6} find a good simulation taking a Fe\textsuperscript{3+} ion in an octahedral symmetry with a \(t_{2g}-e_g\) splitting of 1.6 eV, which is depicted in curve (b) in Fig. 2. For FeO, a good match with the experiment can be found for the Fe\textsuperscript{2+} in an octahedral environment with a splitting of 0.9 eV, see curve (i). The weaker crystal field in FeO, compared with Fe\textsubscript{2}O\textsubscript{3}, is consistent due to its larger Fe–O bond length.

In order to understand the experimental Fe L\textsubscript{2,3} spectrum of Ca\textsubscript{3}FeRhO\textsubscript{6}, we first return to the Fe\textsubscript{2}O\textsubscript{3} spectrum. When we reduce the \(t_{2g}-e_g\) splitting from 1.6 eV (curve b) via 1.0 eV (curve c) to 0.0 eV (curve d), we observe that the the low-energy shoulder becomes washed out, while the high-energy shoulder becomes more pronounced.\textsuperscript{30} Going further to a trigonal crystal field, the high-energy shoulder loses its intensity as shown in curve (e) for a splitting of 0.9 eV between \(d_{\pm 1}\) and \(d_{0}\), and \(d_{0}/d_{\pm 2}\) (\(d_{1xz}/d_{xy}/d_{yz}/d_{xz}\)). The experimental Fe-L\textsubscript{2,3} XAS spectrum of Ca\textsubscript{3}FeRhO\textsubscript{6} in Fig. 2(g) can be well reproduced with this trigonal crystal field of 0.9 eV and in addition a mixing parameter \(V_{\text{mix}} = 0.4\) eV, which mixes the \(d_{z^2}\) with the \(d_{x^2-y^2}\) orbitals; the result for this Fe with the \(3d^5\) high-spin configuration is presented in curve (f).

Figure 2 shows the experimental Fe-L\textsubscript{2,3} XAS spectra of \(g\) Ca\textsubscript{3}FeRhO\textsubscript{6}, along with those of \(a\) Fe\textsubscript{2}O\textsubscript{3} (Fe\textsuperscript{3+}), \(g\) Ca\textsubscript{3}FeRhO\textsubscript{6}, and \(j\) FeO (Fe\textsuperscript{2+}), taken from Park.\textsuperscript{29} together with simulated spectra \(b, c\) in \(O_{h}\), \(d\) spherical, and \(e, f\) \(D_{3h}\) symmetry for Fe\textsuperscript{3+} and simulated spectra in \(h\) \(D_{3h}\) and \(i\) \(O_{h}\) symmetry for Fe\textsuperscript{2+}.
and confirmed by XMCD measurements.

In trigonal-prism symmetry the 3d orbitals are split into $d_{\pm 1}$, $d_0$, and $d_{\pm 2}$ states, see Fig. 4. In terms of one-electron levels, the $d_{\pm 1}$ orbitals lie highest in energy, while the lower lying $d_0$, and $d_{\pm 2}$ usually are nearly degenerate. For a Co$^{3+}$ $d^7$ system, it is a priori not obvious from band structure calculations to say which of these low lying orbitals gets occupied. Details, such as the inclusion of the spin-orbit interaction, can become crucial. Indeed, for Ca$_3$Co$_2$O$_6$, it was found from LDA+U calculations and confirmed by XMCD measurements that the spin-orbit interaction is crucial to stabilize the occupation of the $d_2$ orbital, thereby giving rise to giant orbital moments and Ising-type magnetism. For a Co$^{2+}$ $d^7$ ion, however, the situation is quite different. As we will explain below, the double occupation of the $d_0d_2$ orbitals is energetically much more favored than that of the $d_2d_{-2}$: the energy difference could be of order 1 eV while the $d_0$ and $d_{\pm 2}$ by themselves could be degenerate on a one-electron level. The consequences are straightforward: the double occupation of $d_0d_2$, see Fig. 4(a), should lead to a large orbital moment of $2\mu_B$ (neglecting covalent effects) and Ising type of magnetism with the magnetization direction fixed along the chains. In contrast, the $d_2d_{-2}$, see Fig. 4(b), would have given a quenched orbital moment.

In order to experimentally establish that the Co$^{2+}$ ion has the $d_0d_2$ configuration, we have performed an XMCD study at the Co-$L_{2,3}$ edges of Ca$_3$CoRhO$_6$. Fig. 5 shows the Co-$L_{2,3}$ XMCD spectrum of Ca$_3$CoRhO$_6$ taken at 50 K under 5.5 T. The spectra were taken, respectively, with the photon spin parallel ($\mu^+$, red dotted curve) and antiparallel ($\mu^-$, black solid curve) alignment between photon spin and magnetic field, together with their difference (XMCD) spectrum ($\mu^+ - \mu^-$, blue dashed curve): simulated XMCD spectra for (b) $d_0d_2$ (olive curve) and (c) $d_2d_{-2}$ (magenta curve) minority-spin occupation of the high-spin Co$^{2+}$.

**FIG. 3:** The Co-$L_{2,3}$ spectra of (a) Ca$_3$Co$_2$O$_6$ (Co$^{3+}$), (b) CoO (Co$^{2+}$), and (c) Ca$_3$CoRhO$_6$. The simulated spectra of high-spin Co$^{2+}$ (3d$^7$) in trigonal prismatic symmetry are shown in (d) for a $d_0d_2$ and in (e) for a $d_2d_{-2}$ minority-spin orbital occupation.

**FIG. 4:** Scheme of the two possible 3d occupations for a high-spin Co$^{2+}$ ion in trigonal prismatic symmetry, ignoring the five up spins. (a) The $d_0d_2$ minority-spin occupation allows for a large orbital magnetic moment, whereas (b) for $d_2d_{-2}$ the orbital moment vanishes.
antiparallel ($\mu^-$, black solid curve) to the magnetic field. One can clearly observe large differences between the two spectra with the different alignments. Their difference, $\mu^+ - \mu^-$, is the XMCD spectrum (blue dashed curve).

An important feature of XMCD experiments is that there are sum rules, developed by Thole and Carra et al., to determine the ratio between the orbital ($m_{\text{orb}} = L_z$) and spin ($m_{\text{spin}} = 2S_z$) contributions to the magnetic moment, namely

$$\frac{m_{\text{orb}}}{m_{\text{spin}}} = \frac{2 \Delta L_3 + \Delta L_2}{3 \Delta L_3 - 2 \Delta L_2}. \tag{1}$$

Here, $\Delta L_3$ and $\Delta L_2$ are the energy integrals of the $L_3$ and $L_2$ XMCD intensity. The advantage of these sum rules is that one needs not to do any simulations of the spectra to obtain the desired quantum numbers. In our particular case, we can immediately recognize the presence of a large orbital moment in Fig. 5(a), since there is a large net (negative) integrated XMCD spectral weight. Using Eq. (1) we find $m_{\text{orb}}/m_{\text{spin}} = 0.63$. Since the Co$^{2+}$ ion is quite ionic, $m_{\text{spin}}$ is very close to the expected ionic value of $3\mu_B$. For example, our LDA+U calculations yield $2.72\mu_B$ for the Co$^{2+}$ ion ($2.64\mu_B$ for LDA) and Whangbo et al. obtained $2.71\mu_B$ from GGA calculations. Using a value of $2.7\mu_B$ for the spin moment, we estimate $m_{\text{orb}} = 1.7\mu_B$, in nice agreement with our LDA+U result of $1.69\mu_B$, for the $d_0d_2$ minority-spin orbital occupation.

To critically check our experimental and previous LDA+U results regarding the $d_0d_2$ orbital occupation and the giant orbital moment, we explicitly simulate the experimental XMCD spectra using a charge-transfer configuration-interaction cluster calculation which includes not only the full atomic multiplet theory and the local effects of the solid, but also the oxygen $2p$-cobalt $3d$ hybridization. The results of the calculated Co-$L_{2,3}$ XAS and XMCD spectra are presented in Figs. 3(d) and 5(b), respectively. We can clearly observe that the simulations reproduce the experimental spectra very well. The parameters used are those which indeed give the $d_0d_2$ orbital occupation for the ground state. The magnetic quantum numbers found are $m_{\text{orb}} = 1.65\mu_B$ and $m_{\text{spin}} = 2.46\mu_B$, yielding $m_{\text{orb}}/m_{\text{spin}} = 0.67$ and a total Co magnetic moment of $4.11\mu_B$. With the Rh in the $S = 1/2$ tetravalent state, the total magnetic moment per formula unit should be around $5\mu_B$. This is not inconsistent with the results of the high-field magnetization study by Niitaka et al.: they found a total moment of $4.05\mu_B$, but there the saturation of the magnetization has not yet been reached even under 18.7 Tesla. This can now be understood since the magnetocrystalline anisotropy, associated with the active spin-orbit coupling, is extremely strong and makes it difficult to fully magnetize a powder sample as was used in their study.

We also have simulated the spectra for the $d_2d_{-2}$ scenario. These are depicted in Figs. 3(e) for the XAS and 5(c) for the XMCD. It is obvious that the experimental spectra are not reproduced. The simulated line shapes are very different from the experimental ones and the integral of the simulated XMCD spectrum yields a vanishing orbital moment. We therefore can safely conclude that the ground state of this material is not $d_2d_{-2}$.

For completeness we mention that the magnetic quantum numbers found for this $d_2d_{-2}$ ansatz are $m_{\text{orb}} = 0.03\mu_B$ and $m_{\text{spin}} = 2.86\mu_B$, yielding $m_{\text{orb}}/m_{\text{spin}} = 0.01$ and a
V. STABILITY OF THE $d_{x^2}d_{y^2}$ STATE

Having established that the ground state of Ca$_3$CoRhO$_6$ has the Co$^{2+}$ $d^7$ ion in the doubly occupied $d_{x^2}$ $d_{y^2}$ orbital configuration and not in the $d_{z^2}$ $d_{d^2}$, it is interesting to study its stability in more detail. As already mentioned above, for a Co$^{2+}$ $d^7$ ion, the $d_0$ and $d_{\pm 2}$ states can be energetically very close to each other. For a Co$^{2+}$ $d^7$ ion, however, the $d_0d_2$ and $d_{d^2}$ states are very much different in energy. This is illustrated in the top panel of Fig. 6, in which we have calculated the occupation numbers of the $d_0$, $d_2$, and $d_{\pm 2}$ orbitals as a function of $\Delta_{02}$, the one-electron level splitting between the $d_0$ and $d_{\pm 2}$ orbitals. The $d_0d_2$ ground state which gives the best simulation to the experimental XAS and XMCD spectra was obtained with $\Delta_{02} \approx 0.4$ eV. We can observe that the $d_0d_2$ situation is quite stable for a wide range of $\Delta_{02}$ values, certainly up to 0.8 eV. With a transition region between $\Delta_{02} = 0.8$–1.2 eV, we find a stable $d_{d^2}$–$d_{d^2}$ situation only for $\Delta_{02}$ values larger than 1.2 eV. (For the $d_{d^2}$ simulations above we have used $\Delta_{02} = 1.4$ eV.) This is a very large number indeed, and it can be traced back to the multiplet character of the on-site Coulomb interactions: an occupation of $d_{d^2}$–$d_{d^2}$ means a much stronger overlap of the electron clouds as compared to the case for a $d_0d_2$. This results in a higher repulsion energy, which is not a small quantity in view of the atomic-like values of the $F^2$ and $F^4$ Slater integrals determining the multiplet splitting.

In the middle panel of Fig. 6 we also show the expectation values for $m_{\text{orb}}$ and $m_{\text{spin}}$ when varying $\Delta_{02}$. Again we clearly observe that the large orbital-moment situation is quite stable. To quench the orbital moment one would need much higher $\Delta_{02}$ values. Important is that the spin state does not change here. Bottom panel of Fig. 6 demonstrates that the high-spin state of the Co$^{2+}$ ion is not affected by $\Delta_{02}$: the expectation value $\langle S^2 \rangle$ remains constant throughout at a value consistent with an essentially $S = 3/2$ state. Obviously, the $L^2$ and $J^2$ quantum numbers are strongly affected by $\Delta_{02}$.

VI. CONCLUSION

To summarize, the Rh-$L_{2,3}$, Co-$L_{2,3}$ and Fe-$L_{2,3}$ XAS measurements indicate Co$^{2+}$/Rh$^{4+}$ in Ca$_3$CoRhO$_6$ and Fe$^{3+}$/Rh$^{3+}$ in Ca$_3$FeRhO$_6$. The magnetic properties of Ca$_3$FeRhO$_6$ are relatively simple as both the HS Fe$^{3+}$ and LS Rh$^{3+}$ ions have a closed subshell and thus no orbital degrees of freedom and no orbital moment. The weak intrachain AFM coupling between the HS Fe ions can be understood in terms of the normal superexchange via the intermediate non-magnetic O–Rh–O complex. For Ca$_3$CoRhO$_6$, the combined experimental and theoretical study of the Co-$L_{2,3}$ XAS and XMCD spectra reveals a giant orbital moment of about $1.7 \mu_B$. This large orbital moment is connected with the minority-spin $d_0d_2$ occupation for HS Co$^{2+}$ (3$d^7$) ions in the peculiar trigonal prismatic coordination. The high FM ordering temperature in Ca$_3$CoRhO$_6$, compared with that of Ca$_3$Co$_2$O$_6$, can be attributed to the distinct octahedral sites (which mediate the Co–Co magnetic coupling): the magnetic Rh$^{4+}$ ion ($S = 1/2$) in the former and the nonmagnetic Co$^{3+}$ ion ($S = 0$) in the latter.

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