Insulating state and the importance of the spin-orbit coupling in Ca$_3$CoRhO$_6$

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We have carried out a comparative theoretical study of the electronic structure of the novel one-dimensional Ca$_3$CoRhO$_6$ and Ca$_3$FeRhO$_6$ systems. The insulating antiferromagnetic state for the Ca$_3$FeRhO$_6$ can be well explained by band structure calculations with the closed shell high-spin $d^5$ (Fe$^{3+}$) and low-spin $t_{2g}^6$ (Rh$^{3+}$) configurations. We found for the Ca$_3$CoRhO$_6$ that the Co has a strong tendency to be $d^5$ (Co$^{2+}$) rather than $d^9$ (Co$^{3+}$), and that there is an orbital degeneracy in the local Co electronic structure. We argue that it is the spin-orbit coupling which will lift this degeneracy thereby enabling local spin density approximation + Hubbard U (LSDA+U) band structure calculations to generate the band gap. We predict that the orbital contribution to the magnetic moment in Ca$_3$CoRhO$_6$ is substantial, i.e. significantly larger than 1 $\mu_B$ per formula unit. Moreover, we propose a model for the contrasting intra-chain magnetism in both materials.

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I. INTRODUCTION

The synthesis of the one-dimensional cobaltate Ca$_3$Co$_2$O$_6$ and the discovery of the exotic stair-step jumps in the magnetization at regular intervals of the applied magnetic field have triggered a flurry of research activities, both experimentally and theoretically. This compound consists of [Co$_2$O$_6$]$_\infty$ chains along the c axis of the hexagonal unit cell, with in each chain alternating CoO$_6$ octahedra and CoO$_6$ trigonal prisms. The intra-chain coupling is ferromagnetic (FM) with a Curie temperature of $T_C = 24$ K and the inter-chain antiferromagnetic (AF) with a Néel temperature of $T_N = 10$ K. Owing to an inter-chain magnetic frustration associated with the triangular lattice, the magnetic ground-state is either a partially disordered AF state or a spin-freezing state. Substitution of the Co by other transition metals results in quite dramatic changes of the properties. The Ca$_3$CoRhO$_6$ compound has its $T_C$ shifts up to a high value of 90 K and $T_N$ to 35 K, but the type of its magnetic ground-state is similar to Ca$_3$Co$_2$O$_6$ while Ca$_3$FeRhO$_6$ is an intra-chain AF with $T_N = 12$ K. In these compounds the Rh ions occupy the octahedral sites while the Co/Fe reside within the trigonal prisms.

There is a debate about the electronic structure of these one-dimensional cobaltates in the literature, in particular for Ca$_3$Co$_2$O$_6$ and Ca$_3$CoRhO$_6$. Consensus has yet to arrive about the valence, spin and orbital state of the Co ions, without which one could not make a reliable modeling of the magnetic properties. Focusing on the Ca$_3$CoRhO$_6$ system, it was originally thought that the valence state is Co$^{2+}$/Rh$^{3+}$ based on magnetization measurements and bond valence sum. Subsequent neutron studies concluded, however, that the Co$^{3+}$/Rh$^{3+}$ scenario is a better description. Very recently, a photoemission investigation favors yet the original Co$^{3+}$/Rh$^{4+}$ assignment. Existing band structure calculations also provide a mixed message: a generalized-gradient-approximation (GGA) study suggests the Co$^{3+}$/Rh$^{3+}$ state while an LSDA calculation leaves this issue open. Important is to note that both calculations predict Ca$_3$CoRhO$_6$ to be a metal, in strong disagreement with the experiment.

To resolve these disagreements, we carried out a theoretical study of the electronic structure and magnetic properties of Ca$_3$CoRhO$_6$ in which we took the insulating state of the material as a key finding. For this we applied the LSDA+U method in order to take into account more explicitly the correlated motion of the electrons typical for transition metal oxides. Using Ca$_3$FeRhO$_6$ as a reference, we find that the Co ions have a lower valence than Fe, and that the Co is in an orbitally degenerate state while the Fe are not. The valence assignment coming from our calculations is the Fe$^{3+}$/Rh$^{3+}$ for Ca$_3$FeRhO$_6$ and Co$^{2+}$/Rh$^{4+}$ for Ca$_3$CoRhO$_6$. The insulating state for Ca$_3$FeRhO$_6$ can be readily reproduced, but for Ca$_3$CoRhO$_6$ we infer that the spin-orbit coupling (SOC) must be included in the LSDA+U scheme. We make a testable prediction, namely that there is a large orbital contribution to the magnetic moment in Ca$_3$CoRhO$_6$, about 1.7 $\mu_B$ per formula unit. We also calculate the various exchange constants and propose a model to explain the weak intra-chain AF in Ca$_3$FeRhO$_6$ and enhanced intra-chain FM in Ca$_3$CoRhO$_6$.

II. RESULTS AND DISCUSSION

Our calculations are performed by using the full-potential augmented plane waves plus local orbital method. We took the crystal structure data determined by x-ray diffraction. The muffin-tin sphere radii are chosen to be 2.7, 2.0 and 1.6 Bohr for Ca, Co/Fe/Rh, and O atoms, respectively. The cut-off energy of 16 Ryd is used for plane wave expansion of interstitial wave functions, and 5×5×5 k-mesh for integrations over the Brillouin zone, both of which ensuring a sufficient numeri-
Fig. 1(a) shows the density of states (DOS). One can study in this work the type and origin of the intra-chain pounds behaving like a quasi-one-dimensional system, we separated in the hexagonal $ab$-plane and of these two compounds behaving like a quasi-one-dimensional system, we study in this work the type and origin of the intra-chain magnetic coupling, thereby assuming a FM inter-chain coupling.

As a reference, we first calculate the electronic structure of Ca$_3$FeRhO$_6$ in the FM state using the LSDA. Fig. 1(a) shows the density of states (DOS). One can clearly see that the octahedral Rh 4$d$ has a large $t_{2g}$-$e_g$ crystal-field (CF) splitting of about 3 eV. With the $t_{2g}$ shell completely full and the $e_g$ completely empty, the Rh is formally 3$+$. One can also observe that the Fe 3$d$ spin-up states are essentially completely full and the spin-down completely empty. The Fe is thus formally 3$+$ (3$d^5$) and high-spin (HS, $S=5/2$). The Fe partial DOS also shows that the unoccupied spin-down states are split roughly into two groups with about 1 eV separation. This is caused by the presence of a trigonal CF, making $(d_1, d_{-1})$ orbitals to lie higher than the nearly degenerate $(d_0, d_2, d_{-2})$. Covalency reduces the Fe moment to 3.73 $\mu_B$ but creates at the same time 0.20 $\mu_B$ moment at the Rh and 0.13 $\mu_B$ at each O, so that the total moment is still 5.00 $\mu_B$, see Table I. The material is an insulator, since it is effectively a closed shell system due to the sufficiently large CF splitting at the Rh and exchange splitting on the Fe. We have also calculated the Ca$_3$FeRhO$_6$ in the intra-chain AF state, and found very similar DOS’ses (the spin part not considered). Important is that the total energy of the AF is lower than the FM by about 11 meV (see Table I), explaining why Ca$_3$FeRhO$_6$ is an AF. Our LSDA finding is in close agreement with the GGA results of Vilpesuzanne and Whangbo.

Fig. 1(b) depicts the LSDA results for the Ca$_3$CoRhO$_6$ in the FM state. The DOS shows quite a number of similarities with that of the Ca$_3$FeRhO$_6$, including the large CF at the Rh and the characteristic trigonal CF splitting at the Fe/Co. The only significant difference is the fact that the Co 3$d$ lies lower in energy than the Fe 3$d$, which is reasonable since Co is less electropositive than Fe. The consequences are, however, quite dramatic: the Fermi level now straddles through the $(d_0, d_2, d_{-2})$ part of the Co 3$d$ spin down band, meaning that Ca$_3$CoRhO$_6$ would be a metal. This LSDA result is in clear disagreement with experimental observations. Also Whangbo et al. found a metallic solution. We have investigated the intra-chain AF state for Ca$_3$CoRhO$_6$ and found that it is also metallic. It has, however, a higher energy than the FM by about 106 meV, see Table I. This means that system tends to be FM, at least if one is willing to trust these LSDA results as far as the magnetism is concerned. It is obvious, nevertheless, that this half-metallic solution is an artifact of the LSDA.

The LSDA of Ca$_3$CoRhO$_6$ shows that the Fermi level is located in a narrow Co 3$d$ band with no more than 1 eV width. It is then also natural to expect that already modest electron correlation effects at the Co sites will have a pronounced effect on the energetics of this band. We therefore carried out LSDA+U band structure calculations for both the Ca$_3$CoRhO$_6$ and Ca$_3$FeRhO$_6$ with the Coulomb energy $U$ is set to 5, 4, and 3 eV, and the Hund’s exchange parameter $J_H$ to 0.9, 0.9, 0.5 eV for the Co 3$d$, Fe 3$d$, and Rh 4$d$ shells, respectively.

We will first discuss the results for the Ca$_3$FeRhO$_6$, our reference system. Fig. 2(a) shows the LSDA+U DOS of

![LSDA DOS](image)
Ca$_3$FeRhO$_6$ in the FM state. One can observe that the energy separation between the fully occupied $t_{2g}$ shell and the fully unoccupied $e_g$ has increased in comparison with the LSDA results [Fig. 1(a)], in accordance with the inclusion of $U$. This also happens with the separation between Fe 3$d$ spin-up and spin-down states, whereby the spin-up states are pushed down to about $-7$ eV. This deep-lying state reflects the high stability typical for $3d^5$ ions, in which the high-spin configuration of the half-filled shell gives an energy gain of $4J_H$. With the Fe spin-up states being at the bottom of the valence band, the covalency with the Rh 4$d$ and O 2$p$ bands is much reduced. This is then also reflected in the increase (with respect to LSDA) of the Fe moment to 3.95 $\mu_B$ and decrease of the Rh to 0.11 $\mu_B$ and of each O to 0.11 $\mu_B$. The total magnetic moment should not change: it remains indeed at 5.00 $\mu_B$, see table I. As far as the low energy scale physics is concerned, the band gap has increased from about 0.2 eV to an appreciable 0.9 eV. It does not directly scale with the $U$'s, since it is determined by the occupied Rh $t_{2g}$ and the unoccupied Fe 3$d$ spin-down states. Note that our conclusion that Ca$_3$FeRhO$_6$ is an insulator with HS-Fe$^{3+}$/LS-Rh$^{3+}$ and is a Heisenberg spin-chain system (see below), is $U$-independent.

Calculations for the intra-chain AF state of Ca$_3$FeRhO$_6$ give very similar DOS's (the spin part not considered), with practically the same total energy as the FM (the difference being about 2 meV is within the error bar, see Table I). This and the above LSDA result indicate that the intra-chain AF exchange interaction is very weak. In this situation the effects not included in our calculations, such as the detailed type of inter-chain ordering (we assumed that spins in all neighboring chains are in phase, i.e., we considered FM inter-chain ordering) may start to play a role and may finally determine the type of long-range ordering in Ca$_3$FeRhO$_6$. Thus from the present LSDA+U calculations we can only conclude that the FM and AF intra-chain orderings in this system are practically degenerate. We present below (Section III) qualitative arguments that in reality most probably the intra-chain interaction in Ca$_3$FeRhO$_6$ is weak but AF. All this is not inconsistent with the rather small $T_N$ value of 12 K.

The LSDA+U results for Ca$_3$CoRhO$_6$ are shown in Fig. 2(b). Similar to the Ca$_3$FeRhO$_6$ case, the inclusion of $U$ increases the splitting between the Rh 4$d$ $t_{2g}$ and $e_g$ orbitals as well as Co 3$d$ spin-up and spin-down bands. Also similar is the reduction of the covalency of the 3$d$ spin-up as it is shifted to very low energies. Surprisingly, however, the insulating state is not formed. The Fermi level still straddles through the lower-energy part of the Co 3$d$ spin-down band. The main influence of $U$ here is only that the effective crystal splitting with the $(d_1, -d_1)$ orbitals is increased. To investigate why there is no gap opening, we plot in the inset of Fig. 2(b) a close up of the down-spin Co $d_0$, $d_2$ and $d_{-2}$ states in the vicinity of the Fermi level. We can now observe that the spin-down $d_0$ is fully occupied, and that it is the $d_2$ and $d_{-2}$ bands which are partially occupied. This means first of all, with the spin-up states fully occupied, that the Co ion is essentially in the $d^7$ or 2+ valence state, and not in the $d^6$ or 3+ as proposed recently. Secondly, the inset reveals that it is the degeneracy of the $d_2$ and $d_{-2}$ bands which makes the LSDA+U to be inept in opening the gap. If the $d_0$ were higher in energy than the $d_2$ and $d_{-2}$, or if the Co valence were $3+$, then LSDA+U would certainly have produced a band gap. For completeness, we have also calculated the AF state with the LSDA+U, and found also a metallic state with a 13 meV higher total energy, see Table I.

We propose to include the SOC to lift the $d_{2},d_{-2}$ degeneracy. The use of the SOC to lift the degeneracy in correlated insulators has surprisingly been done only in a few instances. In most cases, this has
been omitted, even for materials for which it is known that the orbital contribution to the magnetic moment is substantial.\textsuperscript{31,34,39,41,42} We claim that the SOC issue is essential for this particular Ca\textsubscript{3}CoRhO\textsubscript{6} compound, motivated also by the report that the magnetocrystalline anisotropy is significant.\textsuperscript{28} Note that for the Co\textsuperscript{2+} ions in Ca\textsubscript{3}CoRhO\textsubscript{6}, the \(d_0\) and \(d_2\)/\(-d_2\) states are split off from the higher-lying \(d_1/d_{-1}\) states by about 1 eV [Fig. 1(b)], i.e., much larger than the SOC energy scale of about 70 meV.\textsuperscript{33} Therefore, the SOC Hamiltonian can be simplified into just \(\zeta_l s_z\) by neglecting the \(l_+s_-\) and \(l_-s_+\) mixing terms, both of which cause a mixing between the \(d_0\) and \(d_1/d_{-1}\), or between the \(d_2\) (\(-d_2\)) and \(d_1\) (\(-d_1\)). Thus, the \(l_z\) and \(s_z\) are good quantum numbers in this particular case.

The results of the LSDA+U+SOC calculations for Ca\textsubscript{3}CoRhO\textsubscript{6} in the intra-chain FM state are shown in Fig. 3. We now can observe that a gap has been opened near the Fermi level, consistent with the experimental finding that the system is an insulator.\textsuperscript{19,16} The band gap is small and is given mainly by the weakly split Rh 4\textit{d} bands. The system is a Mott-Hubbard insulator in which the U in the Rh 4\textit{d} shell is the determining factor.\textsuperscript{28} As far as the Co 3\textit{d} states are concerned, the band gap is about 2 eV, i.e. so large that it no longer determines the band gap of the system. A clearer view is offered in the inset of Fig. 3 which depicts a close up of the down-spin Co \(d_0\), \(d_2\) and \(-d_2\) states in the vicinity of the Fermi level. One can see that the spin-down \(d_2\) band is now fully occupied and the \(-d_2\) fully unoccupied, i.e. there is no partial occupation anymore like in the LSDA+U. Interesting is to note that the spin-down \(d_0\) band has also an unoccupied component slightly above the Fermi level, but not at the Fermi level. This can be attributed to the band formation with the unoccupied Rh 4\textit{d} \(3\textit{z}^2-\textit{r}^2\) state (i.e. \(a_{1g}\) in the trigonal CF), demonstrating the Rh\textsuperscript{4+} valence state with the \(t_{2g}\) configuration and the one-dimensional character along the \(c\)-axis chain.

While the approach to include the SOC is sound in view of the sizable magnetocrystalline anisotropy,\textsuperscript{28} a definitive justification needs to come from a determination of the magnitude of the orbital contribution to the magnetic moment: our LSDA+U+SOC calculations (\(U=5\) eV for Co) predict for the Co\textsuperscript{2+} ions not only a spin moment of 2.72 \(\mu_B\) but especially a very large orbital moment of 1.69 \(\mu_B\) along the \(c\)-axis chain. This is a testable prediction, which is actually confirmed by a recent x-ray magnetic circular dichroism study.\textsuperscript{28} We verified that both the calculated spin and orbital moments stay constant within 0.1 \(\mu_B\) when the \(U\) for Co is varied in the range of 2.5-6 eV. This huge orbital moment and the SOC firmly fix the orientation of the total magnetic moment along the \(c\)-axis chain, and thus the magnetism of Ca\textsubscript{3}CoRhO\textsubscript{6} is highly Ising-like. The calculations also predict an appreciable 0.54 \(\mu_B\) spin moment on the Rh\textsuperscript{4+} 4\textit{d}, and 0.09 \(\mu_B\) on each oxygen, showing the effect of covalency. Note that the Rh\textsuperscript{4+} ions carry no orbital moment, because the one hole resides on the \(a_{1g}\) singlet split off from the \(t_{2g}\) manifold by the trigonal CF. We also note that the Co\textsuperscript{2+}/Rh\textsuperscript{4+} valence state of Ca\textsubscript{3}CoRhO\textsubscript{6}, as we obtained in this work, remain unchanged by counting the electron occupation of the down-spin Co \(d_0\) and \(d_2\) orbitals (the up-spin Co \(d\) shell is fully occupied) and the hole occupation of the down-spin Rh \(d_0\) (i.e. \(a_{1g}\)) orbital, once an insulating gap is opened at \(U >2.5\) eV for Co and \(U >2\) eV for Rh in our LSDA+U calculations including the spin-orbit coupling. All in all, our Co\textsuperscript{2+}/Rh\textsuperscript{4+} solution is thus consistent with the large total magnetic moment as measured by neutron diffraction.\textsuperscript{26,27,30}

We also have carried out LSDA+U+SOC calculations for Ca\textsubscript{3}CoRhO\textsubscript{6} in the intra-chain AF state, and we have found that this state is 70 meV higher in energy than the FM state, see Table I. This allows us to estimate the effective FM exchange parameter of a Co\textsuperscript{2+} pair being 15 meV, using the simple Heisenberg model with the HS-Co\textsuperscript{2+} spin-3/2. These numbers are substantially larger than for the Ca\textsubscript{3}Co\textsubscript{2}O\textsubscript{6} system: there the AF-FM difference is 12 meV and the exchange parameter about 1.5 meV.\textsuperscript{28} Our calculations thus nicely explain why the intra-chain \(T_C\) of Ca\textsubscript{3}CoRhO\textsubscript{6} (90 K) is much higher than that of Ca\textsubscript{3}Co\textsubscript{2}O\textsubscript{6} (24 K). For completeness, we have also carried out LSDA+U+SOC calculations for the Ca\textsubscript{3}FeRhO\textsubscript{6}. The results, however, are almost identical to those of the LSDA+U, since the SOC is not operative for the closed spin-up Fe\textsuperscript{3+} 3\textit{d} shell and the full Rh\textsuperscript{3+} \(t_{2g}\) state. The absence of an orbital moment accounts for its Heisenberg spin character and very weak magnetocrystalline anisotropy.\textsuperscript{31}
TABLE I: Calculated electronic states of Ca₃FeRhO₆ and Ca₃CoRhO₆ (FM: ferromagnetic; AF: antiferromagnetic; -I:insulator; -M:metal); total energy (meV) per formula unit relative to the ground state; spin moments (μB) at each Fe/Co, Rh, and O ion, as well as in the interstitial region and total magnetic moment per formula unit. Only the Co has the orbital moment and is shown. The Ca spin moment is about 0.01 μB and the Fe orbital moment 0.02 μB, and are thus omitted.

| System          | State   | Energy | Fe | Rh | O | Interstitial | Total     | Figure |
|-----------------|---------|--------|----|----|---|-------------|-----------|--------|
| LSDA            | FM-I    | 11     | 3.73 | 0.20 | 0.13 | 0.27 | 5.00 | Fig. 1(a) |
| LSDA            | AF-I    | 0      | ±3.72 | 0 | ±0.12 | 0 | 0 |        |
| LSDA+U          | FM-I    | 0      | 3.95 | 0.11 | 0.11 | 0.23 | 5.00 | Fig. 2(a) |
| LSDA+U          | AF-I    | 2      | ±3.95 | 0 | ±0.11 | 0 | 0 |        |
| Ca₃CoRhO₆       | state   | energy | Co | Co₃g+½ | Rh | O | interstitial | total     | Figure |
| LSDA            | FM-M    | 0      | 2.64 | 0.37 | 0.13 | 0.16 | 4.00 | Fig. 1(b) |
| LSDA            | AF-M    | 106    | ±2.63 | 0 | ±0.12 | 0 | 0 |        |
| LSDA+U          | FM-M    | 0      | 2.85 | 0.23 | 0.13 | 0.15 | 4.00 | Fig. 2(b) |
| LSDA+U          | AF-M    | 13     | ±2.87 | 0 | ±0.11 | 0 | 0 |        |
| LSDA+U+SOC      | FM-I    | 0      | 2.72 | 1.69 | 0.54 | 0.09 | 0.18 | 5.69 | Fig. 3 |
| LSDA+U+SOC      | AF-I    | 70     | 2.73, -2.53 | 1.69, -1.70 | 0.55 | 0.09, -0.01 | 0.07 | 1.00 |        |

III. MODEL OF MAGNETISM

In order to explain both the experimentally observed and theoretically (computationally) confirmed weak intrachain AF (T_N=12 K) in Ca₃FeRhO₆ and relatively strong FM (T_C=90 K) in Ca₃CoRhO₆, we propose the following model. Starting from our finding that Ca₃FeRhO₆ has the HS Fe³⁺ and LS Rh³⁺ (non-magnetic t₂g⁶) valence state, a charge fluctuation will create the Fe²⁺/Rh⁴⁺ pair rather than Fe⁴⁺/Rh²⁺, since it is easier to stabilize a Rh⁴⁺ rather than an Fe⁴⁺. In Fig. 4(a), we sketch the normal superexchange mechanism Fe⁴⁺-(O²⁻)-Rh³⁺-(O²⁻)-Fe³⁺ via the intermediate non-magnetic Rh³⁺ (in the figure the O²⁻ is omitted for clarity). Since the HS Fe³⁺ has a closed up-spin 3d shell, only the down-spin Rh³⁺ electron [e.g., the a₁g (3z²-r²)] can make a virtual excitation, which naturally explains the intra-chain AF, with a low T_N due to the large Fe-Fe distance of 5.39 Å. In fact, this result is a direct analog of the first Goodenough-Kanamori-Anderson rule.\[46\] In addition to the spin-triplet oxygen-hole mediated intra-chain FM ordering present in both Ca₃CoRhO₆ and Ca₃Co₂O₆,\[23\] this mechanism accounts for a higher T_C in the former than in the latter. Note that if Ca₃CoRhO₆ had the HS Co³⁺ and LS non-magnetic Rh³⁺ valence states, as in the case of Ca₃Co₂O₆ with the HS trigonal Co²⁺ and LS non-magnetic octahedral Co³⁺, its T_C would be lower than that of Ca₃Co₂O₆ due to a longer distance between the magnetic HS Co³⁺ ions in the former than latter.

IV. CONCLUSION

In summary, we have performed systematic LSDA and LSDA+U calculations with the inclusion of the spin-orbit coupling for the new quasi-one-dimensional spin-chain materials Ca₃FeRhO₆ and Ca₃CoRhO₆. We conclude that Ca₃CoRhO₆ is a Mott insulator with the high-spin Co²⁺ and low-spin Rh⁴⁺ configurations, and that the correlated insulator Ca₃FeRhO₆ has the closed-shell high-spin Fe³⁺ and low-spin Rh²⁺. We predict that Ca₃CoRhO₆ has a very large orbital moment at the Co²⁺ site, which also explains the strong magnetocrystalline anisotropy and the highly Ising-like behavior. The inclusion of the spin-orbit coupling in the present LSDA+U calculations is also crucial to obtain the insulating state. This highlights the importance of the spin-orbit coupling in (nearly) degenerate correlated sys-
tems. In contrast, Ca$_3$FeRhO$_6$ has spin-only moments and behaves like a Heisenberg spin-chain system. Moreover, our calculations reproduce the relatively strong ferromagnetic intra-chain coupling in Ca$_3$CoRhO$_6$ but the weak, presumably antiferromagnetic one in Ca$_3$FeRhO$_6$, and we propose a model to explain the contrasting magnetism.

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18. Using LSDA+U+SOC calculations for two configuration states of the high-spin Co$^{2+}$ ions in Ca$_3$CoRhO$_6$, i.e. the minority-spin $d_{5g}$ (the ground state, see more in the main text) and $d_{6g}$ (a metastable state), we obtained the total-energy difference of 142 meV/Co between them, which is twice the SOC constant. Then the SOC constant is calculated to be 71 meV. This is a commonly accepted value and agrees well with a Hartree-Fock value of 66 meV (M. W. Haverkort, PhD thesis, University of Cologne, 2005; [http://xxx.lanl.gov/abs/cond-mat/0505214](http://xxx.lanl.gov/abs/cond-mat/0505214)).
Z. Hu et al., to be published; see also the presentation TT 25.96 at the Spring Meeting of The German Physical Society, March 2006 (website: http://www.dpg-tagung.de/archive/2006/dresden/tt25.pdf). Note also that our previous prediction of a huge orbital moment in the isostructural Ca$_3$Co$_2$O$_6$ (Ref. 23) was already confirmed experimentally [T. Burnus et al., Phys. Rev. B 74, 245111 (2006)].

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