PHYSICAL REVIEW B **75**, 245118 (2007)

Insulating state and the importance of the spin-orbit coupling in Ca_3CoRhO_6

Hua Wu, Z. Hu, D. I. Khomskii, and L. H. Tjeng

II. Physikalisches Institut, Universität zu Köln, Zülpicher Strasse 77, D-50937 Köln, Germany

(Received 23 July 2006; revised manuscript received 23 March 2007; published 20 June 2007; publisher error corrected 21 June 2007)

We have carried out a comparative theoretical study of the electronic structure of the one-dimensional Ca_3CoRhO_6 and Ca_3FeRhO_6 systems. The insulating antiferromagnetic state for Ca_3FeRhO_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 Ca_3CoRhO_6 that Co has a strong tendency to be d^7 (Co^{2+}) rather than d^6 (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 band structure calculations to generate the band gap. We predict that the orbital contribution to the magnetic moment in Ca_3CoRhO_6 is substantial, i.e., significantly larger than 1 μ_B/f.u.. Moreover, we propose a model to explain the contrasting intrachain magnetism in both materials.

DOI: 10.1103/PhysRevB.75.245118 PACS number(s): 71.20.−b, 71.70.−d, 75.25.+z, 75.30.Gw

I. INTRODUCTION

The synthesis of one-dimensional cobaltate $Ca_3Co_2O_6$ (Refs. 1 and 2) and the discovery of the exotic stair-step jumps in the magnetization at regular intervals of the applied magnetic field[3,4] have triggered a flurry of research activities, both experimentally[4–16] and theoretically.[17–24] This compound consists of $[Co_2O_6]_\infty$ chains running along the c axis of the hexagonal unit cell, with alternating CoO_6 octahedra and CoO_6 trigonal prisms in each chain.[1] The intrachain coupling is ferromagnetic (FM) with a Curie temperature of T_C=24 K and the interchain antiferromagnetic (AF) with a Néel temperature of T_N=10 K.[3] Owing to an interchain magnetic frustration associated with the triangular lattice, the magnetic ground state is either a partially disordered AF state or a spin-freezing state.[3] Substitution of Co by other transition metals results in quite dramatic changes of the properties. The Ca_3CoRhO_6 compound has its T_C shifts up to a high value of 90 K and T_N to 35 K,[25–30] but the type of its magnetic ground state is similar to $Ca_3Co_2O_6$,[26,27] while Ca_3FeRhO_6 is an intrachain AF with T_N=12 K.[25,29,31] In these compounds, the Rh ions occupy the octahedral sites while the Co/Fe ions reside within the trigonal prisms.[25,29]

There is a debate about the electronic structure of these one-dimensional cobaltates in the literature, in particular, for $Ca_3Co_2O_6$ (Refs. 1–23) and Ca_3CoRhO_6.[16,17,25–30,32] 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_3CoRhO_6 system, it was originally thought that the valence state is Co^{2+}/Rh^{4+} based on magnetization measurements and bond valence sum.[25,26] Subsequent neutron studies concluded, however, that the Co^{3+}/Rh^{3+} scenario is a better description.[27,30] Very recently, a photoemission investigation favors yet the original Co^{2+}/Rh^{4+} assignment.[16] Existing band structure calculations also provide a mixed message: a generalized-gradient-approximation (GGA) study suggests the Co^{3+}/Rh^{3+} state,[17] while a local spin density approximation (LSDA) calculation leaves this issue open.[32] It is important to note that both calculations predict Ca_3CoRhO_6 to be a metal, in strong disagreement with the experiment.[10,16]

To resolve these disagreements, we carried out a theoretical study of the electronic structure and magnetic properties of Ca_3CoRhO_6 in which we took the insulating state of the material[10,16] as a key finding. For this, we applied the LSDA+U method[33,34] in order to take into account more explicitly the correlated motion of the electrons typical for transition metal oxides. Using Ca_3FeRhO_6 as a reference, we find that the Co ions have a lower valence than Fe and that Co are in an orbitally degenerate state while Fe are not. The valence assignment coming from our calculations is Fe^{3+}/Rh^{3+} for Ca_3FeRhO_6 and Co^{2+}/Rh^{4+} for Ca_3CoRhO_6. The insulating state for Ca_3FeRhO_6 can be readily reproduced, but for Ca_3CoRhO_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_3CoRhO_6, about 1.7 μ_B/f.u. We also calculate the various exchange constants and propose a model to explain the weak intrachain AF in Ca_3FeRhO_6 and enhanced intrachain FM in Ca_3CoRhO_6.

II. RESULTS AND DISCUSSION

Our calculations are performed by using the full-potential augmented plane waves plus local orbital method.[35] We took the crystal structure data determined by x-ray diffraction.[25] 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 cutoff energy of 16 Ry is used for plane wave expansion of interstitial wave functions and $5\times5\times5$ **k** mesh for integrations over the Brillouin zone, both of which ensuring a sufficient numerical accuracy. The SOC is included by second-variational method with the scalar relativistic wave functions,[35] and actually l_z and s_z are good quantum numbers due to the special trigonal crystal field of the Co sites as seen below. The easy magnetization direction is along the c-axis chains. In view of those c-axis chains being well 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 intrachain magnetic coupling, thereby assuming a FM interchain coupling.

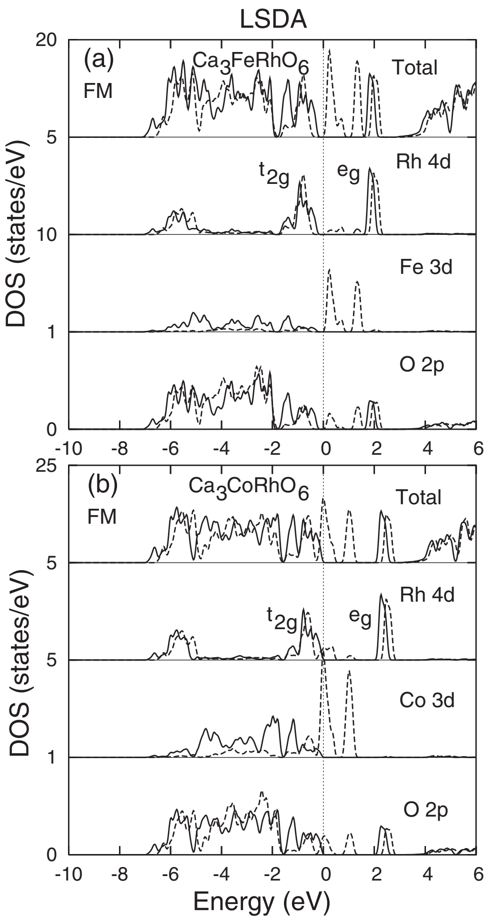

FIG. 1. Density of states (DOS) of Ca_3FeRhO_6 [panel (a)] and Ca_3CoRhO_6 [panel (b)] in the ferromagnetic (FM) state from LSDA. The Fermi level is set at zero energy. Both panels show, from top to bottom, the total DOS, the Rh 4*d*, Fe/Co 3*d*, and O 2*p* partial DOS. Solid (dashed) lines depict the spin-up (-down) states.

As a reference, we first calculate the electronic structure of Ca_3FeRhO_6 in the FM state using the LSDA. Figure 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.[36] With the t_{2g} shell completely full and the e_g completely empty, Rh is formally $3+(4d^6)$ and takes the low-spin (LS, $S=0$) state. One can also observe that the Fe 3*d* spin-up states are essentially completely full and the spin-down states completely empty. Fe is thus formally $3+(3d^5)$ 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}).[2,17–23] Covalency reduces the Fe moment to 3.73 μ_B but creates at the same time 0.20 μ_B moment at the Rh and 0.13 μ_B at each O, so that the total moment is still 5.00 μ_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 Rh and exchange splitting on Fe. We have also calculated Ca_3FeRhO_6 in the intrachain AF state and found very similar DOSs (the spin part not considered). It is important to note that the total energy of the AF is lower than the FM by about 11 meV (see Table I), explaining why Ca_3FeRhO_6 is an AF. Our LSDA finding is in close agreement with the GGA results of Villesuzanne and Whangbo.[22]

Figure 1(b) depicts the LSDA results for Ca_3CoRhO_6 in the FM state. The DOS shows quite a number of similarities with that of Ca_3FeRhO_6, including the large CF at Rh and the characteristic trigonal CF splitting at Fe/Co. The only significant difference is the fact that Co 3*d* lies lower in energy than 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_3CoRhO_6 would be a metal. This LSDA result is in clear

TABLE I. Calculated electronic states of Ca_3FeRhO_6 and Ca_3CoRhO_6 (FM: intrachain ferromagnetic, AF: intrachain antiferromagnetic, -I: insulator, and -M: metal); total energy (meV) per formula unit relative to the ground state; spin moments (μ_B) at each Fe/Co, Rh, and O ion, as well as in the interstitial region and total magnetic moment per formula unit. Only Co has the orbital moment and is shown. The Ca spin moment is about 0.01μ_B and the Fe orbital moment 0.02μ_B, and are thus omitted.

Ca_3FeRhO_6	State	Energy	Fe		Rh	O	Interstitial	Total	Figure
LSDA	FM-I	11	3.73		0.20	0.13	0.27	5.00	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	2(a)
LSDA+U	AF-I	2	±3.95		0	±0.11	0	0	
Ca_3CoRhO_6	State	Energy	Co	Co^{orb}	Rh	O	Interstitial	Total	Figure
LSDA	FM-M	0	2.64		0.37	0.13	0.16	4.00	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	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	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	

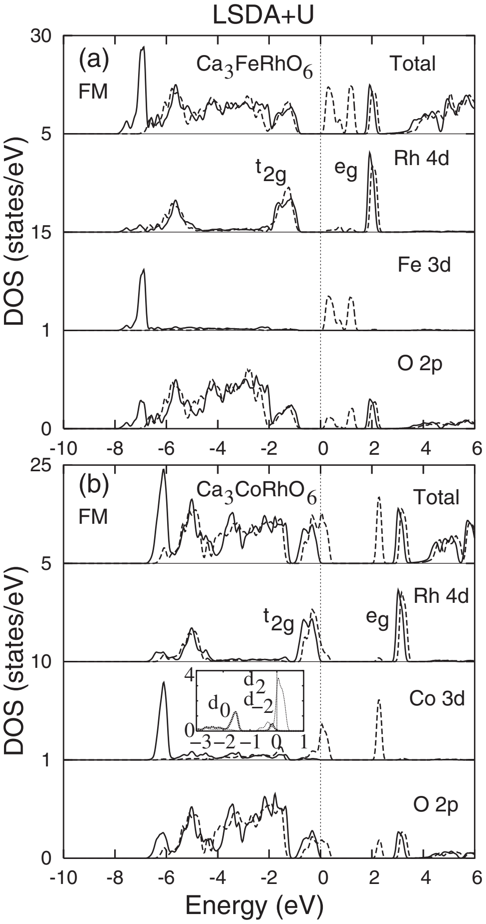

FIG. 2. Density of states (DOS) of Ca_3FeRhO_6 [panel (a)] and Ca_3CoRhO_6 [panel (b)] in the ferromagnetic (FM) state from LSDA+U. Inset: Close-up of the down-spin Co d_0, d_2, and d_{-2} DOS. See Fig. 1 caption for other notations.

disagreement with experimental observations.[10,16] Also, Whangbo *et al.*[17] found a metallic solution. We have investigated the intrachain AF state for Ca_3CoRhO_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_3CoRhO_6 shows that the Fermi level is located in a narrow Co $3d$ band with not 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[34] for both Ca_3CoRhO_6 and Ca_3FeRhO_6 with the Coulomb energy U sets to 5, 4, and 3 eV, and Hund's exchange parameter J_H to 0.9, 0.9, and 0.5 eV for the Co $3d$, Fe $3d$, and Rh $4d$ shells, respectively.

We will first discuss the results for Ca_3FeRhO_6, our reference system. Figure 2(a) shows the LSDA+U DOS of Ca_3FeRhO_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 $3d$ 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 $4d$ and O $2p$ bands is much reduced. This is then also reflected in the increase (with respect to LSDA) of the Fe moment to 3.95 μ_B and decrease of the Rh moment to 0.11 μ_B and of each O to 0.11 μ_B. The total magnetic moment should not change: it remains indeed at 5.00 μ_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 $3d$ spin-down states. Note that our conclusion that Ca_3FeRhO_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 intrachain AF state of Ca_3FeRhO_6 give very similar DOSs (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 intrachain AF exchange interaction is very weak. In this situation, the effects not included in our calculations, such as the detailed type of interchain ordering (we assumed that spins in all neighboring chains are in phase, i.e., we considered FM interchain ordering), may start to play a role and may finally determine the type of long-range ordering in Ca_3FeRhO_6. Thus, from the present LSDA+U calculations, we can only conclude that the FM and AF intrachain orderings in this system are practically degenerate. We present below (Sec. III) qualitative arguments that in reality most probably the intrachain interaction in Ca_3FeRhO_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_3CoRhO_6 are shown in Fig. 2(b). Similar to the Ca_3FeRhO_6 case, the inclusion of U increases the splitting between the Rh $4d$ t_{2g} and e_g orbitals as well as Co $3d$ spin-up and spin-down bands. Also, similar is the reduction of the covalency of the $3d$ 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 $3d$ spin-down band. The main influence of U here is only that the effective level 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.[17,27,30] Secondly, the inset reveals that it is the degeneracy of the d_2 and d_{-2} bands which makes the LSDA+U to be inoperative to open 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

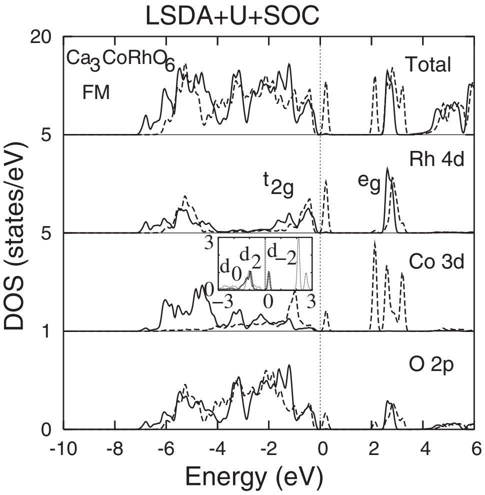

FIG. 3. Density of states (DOS) of Ca_3CoRhO_6 in the ferromagnetic (FM) state from LSDA+U+SOC. Inset: Close-up of the down-spin Co d_0, d_2, and d_{-2} DOS. See Fig. 1 caption for other notations.

the AF state with the LSDA+U and also found 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.[37,38] 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.[33,39–42] We claim that the SOC issue is essential for this particular Ca_3CoRhO_6 compound, also motivated by the report that the magnetocrystalline anisotropy is significant.[26] Note that for the Co^{2+} ions in Ca_3CoRhO_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.[43] Therefore, the SOC Hamiltonian can be simplified into just $\zeta l_z s_z$ 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_3CoRhO_6 in the intrachain FM state are shown in Fig. 3. We can now observe that a gap has been opened near the Fermi level, consistent with the experimental finding that the system is an insulator.[10,16] The band gap is small and is given mainly by the weakly split Rh 4*d* bands. The system is a Mott-Hubbard insulator in which the U in the Rh 4*d* shell is the determining factor.[44] As far as the Co 3*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. It is interesting 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*d* $3z^2-r^2$ state (i.e., a_{1g} in the trigonal CF), demonstrating the Rh^{4+} valence state with the t_{2g}^5 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,[26] a definitive justification can 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^{2+} ions not only a spin moment of 2.72 μ_B but especially a very large orbital moment of 1.69 μ_B along the *c*-axis chain. This is a testable prediction, which is actually confirmed by a recent x-ray magnetic circular dichroism study.[45] We verified that both the calculated spin and orbital moments stay constant within 0.1 μ_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_3CoRhO_6 is highly Ising-like. The calculations also predict an appreciable 0.54 μ_B spin moment on the Rh^{4+} 4*d*, and 0.09 μ_B on each oxygen, showing the effect of covalency. Note that the Rh^{4+} ions carry no orbital moment, because the one hole resides on the a_{1g} singlet splitoff from the t_{2g} manifold by the trigonal CF. We also note that the Co^{2+}/Rh^{4+} valence state of Ca_3CoRhO_6, as we obtained in this work, remains 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^{2+}/Rh^{4+} solution is thus consistent with the large total magnetic moment as measured by neutron diffraction.[26,27,30]

We have also carried out LSDA+U+SOC calculations for Ca_3CoRhO_6 in the intrachain 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^{2+} pair being 15 meV, using the simple Heisenberg model with the HS-Co^{2+} spin-3/2. These numbers are substantially larger than for the $Ca_3Co_2O_6$ system: there the AF-FM difference is 12 meV and the exchange parameter about 1.5 meV.[23] Our calculations thus nicely explain why the intrachain T_C of Ca_3CoRhO_6 (90 K) is much higher than that of $Ca_3Co_2O_6$ (24 K). For completeness, we have also carried out LSDA+U+SOC calculations for Ca_3FeRhO_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^{3+} 3*d* shell and the full Rh^{3+} t_{2g}^6 state. The absence of an orbital moment accounts for its Heisenberg spin character and very weak magnetocrystalline anisotropy.[31]

III. MODEL OF MAGNETISM

In order to explain both the experimentally observed and theoretically (computationally) confirmed weak intrachain AF (T_N=12 K) in Ca_3FeRhO_6 and relatively strong FM (T_C=90 K) in Ca_3CoRhO_6, we propose the following model. Starting from our finding that Ca_3FeRhO_6 has the HS-Fe^{3+} and LS-Rh^{3+} (nonmagnetic t_{2g}^6) valence state, a

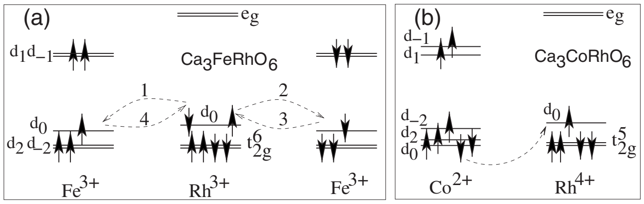

FIG. 4. Model of the intrachain AF in Ca_3FeRhO_6 (a) and of the intrachain FM in Ca_3CoRhO_6 (b).

charge fluctuation will create the Fe^{2+}/Rh^{4+} pair rather than Fe^{4+}/Rh^{2+}, since it is easier to stabilize Rh^{4+} than Fe^{4+}. In Fig. 4(a), we sketch the normal superexchange mechanism Fe^{3+}-(O^{2-})-Rh^{3+}-(O^{2-})-Fe^{3+} via the intermediate nonmagnetic Rh^{3+} (in the figure, O^{2-} is omitted for clarity). Since HS-Fe^{3+} has a closed up-spin $3d$ shell, only the down-spin Rh^{3+} electron [e.g., the a_{1g} $(3z^2-r^2)$] can make a virtual excitation, which naturally explains the intrachain 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]

Ca_3CoRhO_6, in contrast, has the HS-Co^{2+} and LS-Rh^{4+} (t^5_{2g}, $S=1/2$) valence state. We therefore consider the Co^{3+}/Rh^{3+} charge fluctuation (rather than the Co^{1+}/Rh^{5+} charge fluctuation with a rarely observed Co^{1+} state) for the virtual excitation path Co^{2+}-(O^{2-})-Rh^{4+}. Since Rh^{4+} has a large $t_{2g}-e_g$ CF splitting which makes the empty e_g states to be costly to reach, it will be the t^5_{2g} states which will allow for an electron transfer to the empty down-spin a_{1g} orbital, as shown in Fig. 4(b). If Co^{2+} and Rh^{4+} have a FM alignment, the down-spin Co^{2+} a_{1g} (d_0) electron will do so; otherwise (in the AF Co^{2+}/Rh^{4+} alignment), the spin-up a_{1g} electron will do, but obviously with a higher-energy cost than the former by three times Hund's exchange energy of the Co ion. Thus, Co^{2+} and Rh^{4+} strongly prefer the FM alignment, being an analog of the second Goodenough-Kanamori-Anderson rule.[46] In addition to the spin-triplet oxygen-hole mediated intrachain FM ordering present in both Ca_3CoRhO_6 and $Ca_3Co_2O_6$,[23] this mechanism accounts for a higher T_C in the former than in the latter. Note that if Ca_3CoRhO_6 had the HS-Co^{3+} and LS nonmagnetic Rh^{3+} valence states, as in the case of $Ca_3Co_2O_6$ with the HS trigonal Co^{3+} and LS nonmagnetic octahedral Co^{3+}, its T_C would be lower than that of $Ca_3Co_2O_6$ due to a longer distance between the magnetic HS-Co^{3+} ions in the former than the latter.

IV. CONCLUSION

In summary, we have performed systematic LSDA and LSDA+U calculations with the inclusion of the spin-orbit coupling for the quasi-one-dimensional spin-chain materials Ca_3FeRhO_6 and Ca_3CoRhO_6. We conclude that Ca_3CoRhO_6 is a Mott insulator with the high-spin Co^{2+} and low-spin Rh^{4+} configurations and that correlated insulator Ca_3FeRhO_6 has closed-shell high-spin Fe^{3+} and low-spin Rh^{3+}. We predict that Ca_3CoRhO_6 has a very large orbital moment at the Co^{2+} site, which also explains the strong magnetocrystalline anisotropy and the highly Ising-spin-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 systems. In contrast, Ca_3FeRhO_6 has spin-only moments and behaves like a Heisenberg spin-chain system. Moreover, our calculations reproduce the relatively strong ferromagnetic intrachain coupling in Ca_3CoRhO_6 but the weak, presumably antiferromagnetic one in Ca_3FeRhO_6, and we propose a model to explain the contrasting magnetism.

ACKNOWLEDGMENTS

We thank M. W. Haverkort and T. Burnus for valuable discussions. This work is supported by the Deutsche Forschungsgemeinschaft through SFB 608 and by the European project COMEPHS.

---

[1] H. Fjellvåg, E. Gulbrandsen, S. Aasland, A. Olsen, and B. Hauback, J. Solid State Chem. **124**, 190 (1996).

[2] S. Aasland, H. Fjellvåg, and B. Hauback, Solid State Commun. **101**, 187 (1997).

[3] H. Kageyama, K. Yoshimura, K. Kosuge, H. Mitamura, and T. Goto, J. Phys. Soc. Jpn. **66**, 1607 (1997).

[4] A. Maignan, C. Michel, A. C. Masset, C. Martin, and B. Raveau, Eur. Phys. J. B **15**, 657 (2000).

[5] H. Kageyama, K. Yoshimura, K. Kosuge, M. Azuma, M. Takano, H. Mitamura, and T. Goto, J. Phys. Soc. Jpn. **66**, 3996 (1997).

[6] B. Martínez, V. Laukhin, M. Hernando, J. Fontcuberta, M. Parras, and J. M. González-Calbet, Phys. Rev. B **64**, 012417 (2001).

[7] B. Raquet, M. N. Baibich, J. M. Broto, H. Rakoto, S. Lambert, and A. Maignan, Phys. Rev. B **65**, 104442 (2002).

[8] S. Rayaprol, K. Sengupta, and E. V. Sampathkumaran, Solid State Commun. **128**, 79 (2003).

[9] V. Hardy, S. Lambert, M. R. Lees, and D. McK. Paul, Phys. Rev. B **68**, 014424 (2003).

[10] A. Maignan, S. Hébert, C. Martin, and D. Flahaut, Mater. Sci. Eng., B **104**, 121 (2003).

[11] A. Maignan, V. Hardy, S. Hébert, M. Drillon, M. R. Lees, O. Petrenko, D. Mc K. Paul, and D. Khomskii, J. Mater. Chem. **14**, 1231 (2004).

[12] E. V. Sampathkumaran, N. Fujiwara, S. Rayaprol, P. K. Madhu, and Y. Uwatoko, Phys. Rev. B **70**, 014437 (2004).

[13] D. Flahaut, A. Maignan, S. Hébert, C. Martin, R. Retoux, and V. Hardy, Phys. Rev. B **70**, 094418 (2004).

[14] T. Sekimoto, S. Noguchi, and T. Ischida, J. Phys. Soc. Jpn. **73**, 3217 (2004).

[15] V. Hardy, D. Flahaut, M. R. Lees, and O. A. Petrenko, Phys. Rev. B **70**, 214439 (2004).

[16] K. Takubo, T. Mizokawa, S. Hirata, J.-Y. Son, A. Fujimori, D.

Topwal, D. D. Sarma, S. Rayaprol, and E.-V. Sampathkumaran, Phys. Rev. B **71**, 073406 (2005).

[17] M.-H. Whangbo, D. Dai, H.-J. Koo, and S. Jobic, Solid State Commun. **125**, 413 (2003).

[18] R. Vidya, P. Ravindran, H. Fjellvåg, A. Kjekshus, and O. Eriksson, Phys. Rev. Lett. **91**, 186404 (2003).

[19] V. Eyert, C. Laschinger, T. Kopp, and R. Frésard, Chem. Phys. Lett. **385**, 249 (2004).

[20] R. Frésard, C. Laschinger, T. Kopp, and V. Eyert, Phys. Rev. B **69**, 140405(R) (2004).

[21] D. Dai and M.-H. Whangbo, Inorg. Chem. **44**, 4407 (2005).

[22] A. Villesuzanne and M.-H. Whangbo, Inorg. Chem. **44**, 6339 (2005).

[23] H. Wu, M. W. Haverkort, Z. Hu, D. I. Khomskii, and L. H. Tjeng, Phys. Rev. Lett. **95**, 186401 (2005).

[24] Y. B. Kudasov, Phys. Rev. Lett. **96**, 027212 (2006).

[25] S. Niitaka, H. Kageyama, M. Kato, K. Yoshimura, and K. Kosuge, J. Solid State Chem. **146**, 137 (1999).

[26] S. Niitaka, H. Kageyama, K. Yoshimura, K. Kosuge, S. Kawano, N. Aso, A. Mitsuda, H. Mitamura, and T. Goto, J. Phys. Soc. Jpn. **70**, 1222 (2001).

[27] S. Niitaka, K. Yoshimura, K. Kosuge, M. Nishi, and K. Kakurai, Phys. Rev. Lett. **87**, 177202 (2001).

[28] E. V. Sampathkumaran and A. Niazi, Phys. Rev. B **65**, 180401(R) (2002).

[29] M. J. Davis, M. D. Smith, and H.-C. zur Loye, J. Solid State Chem. **173**, 122 (2003).

[30] M. Loewenhaupt, W. Schäfer, A. Niazi, and E. V. Sampathkumaran, Europhys. Lett. **63**, 374 (2003).

[31] S. Niitaka, K. Yoshimura, K. Kosuge, K. Mibu, H. Mitamura, and T. Goto, J. Magn. Magn. Mater. **260**, 48 (2003).

[32] V. Eyert, U. Schwingenschlögl, C. Hackenberger, T. Kopp, R. Frésard, and U. Eckern, e-print arXiv:cond-mat/0509374.

[33] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991).

[34] V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyżyk, and G. A. Sawatzky, Phys. Rev. B **48**, 16929 (1993).

[35] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, http://www.wien2k.at

[36] Actually, in both Ca_3FeRhO_6 and Ca_3CoRhO_6, octahedral Rh feels a trigonal crystal field. However, the a_{1g} singlet splitoff from the t_{2g} manifold lies above the e_g^{π} doublet only by about 200 (230) meV in Ca_3FeRhO_6 (Ca_3CoRhO_6), being much less than the cubic $t_{2g}-e_g$ splitting of about 3 eV. Therefore, we keep to use in this work the conventional orbital index t_{2g}.

[37] I. V. Solovyev, A. I. Liechtenstein, and K. Terakura, Phys. Rev. Lett. **80**, 5758 (1998).

[38] J. Kuneš, H. Rosner, D. Kasinathan, C. O. Rodriguez, and W. E. Pickett, Phys. Rev. B **68**, 115101 (2003).

[39] I. I. Mazin and V. I. Anisimov, Phys. Rev. B **55**, 12822 (1997).

[40] I. Leonov, A. N. Yaresko, V. N. Antonov, M. A. Korotin, and V. I. Anisimov, Phys. Rev. Lett. **93**, 146404 (2004).

[41] H.-T. Jeng, G. Y. Guo, and D. J. Huang, Phys. Rev. Lett. **93**, 156403 (2004).

[42] M. Cococcioni and S. de Gironcoli, Phys. Rev. B **71**, 035105 (2005).

[43] Using LSDA+U+SOC calculations for two configuration states of the high-spin Co^{2+} ions in Ca_3CoRhO_6, i.e., the minority-spin d_0d_2 (the ground state, see more in the main text) and d_0d_{-2} (a metastable state), we obtained the total-energy difference of 142 meV/Co between them, which is two times 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, Ph.D. thesis, University of Cologne, 2005; http://xxx.lanl.gov/abs/cond-mat/0505214).

[44] J. Zaanen, G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. **55**, 418 (1985).

[45] Z. Hu *et al.* (unpublished); see also the presentation TT 25.96 at the Spring Meeting of The German Physical Society, March 2006 (unpublished), website: http://www.dpg-tagung.de/archive/2006/dresden//t25.pdf. Note also that our previous prediction of a huge orbital moment in the isostructural $Ca_3Co_2O_6$ (Ref. 23) was already confirmed experimentally [T. Burnus *et al.*, Phys. Rev. B **74**, 245111 (2006)].

[46] J. B. Goodenough, in *Magnetism and the Chemical Bond* (Interscience Publishers, New York-London, 1963).