Evaluation of half-metallic antiferromagnetism in A_2CrFeO$_6$ (A = La, Sr)

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The nearly well-ordered double perovskite La$_2$CrFeO$_6$ has been synthesized recently. Contrary to previous theoretical predictions, but in agreement with experimental observations, our first principle calculations indicate an insulating ferrimagnet La$_2$CrFeO$_6$ with antialigned $S = 3/2$ Cr^{3+} and $S = 5/2$ Fe^{3+} ions, using the local spin density approximation (LSDA), a correlated band theory LDA + U, and the Tran-Blaha modified Becke-Johnson method. Additionally, we investigated the double perovskite Sr$_2$CrFeO$_6$, which is as yet unsynthesized. In LSDA calculations, this system shows formally tetravalent Cr and Fe ions both having antialigned $S = 1$ moments, but is a simple metal. Once applying on-site Coulomb repulsion U on both Cr and Fe ions, this system becomes half metallic and the moment of Fe is substantially reduced, resulting in zero net moment. These results are consistent with our fixed spin moment studies. Our results suggest a precisely compensated half-metallic Sr$_2$CrFeO$_6$.

I. INTRODUCTION

A half-metallic antiferromagnet has one conducting spin channel and the other insulating spin channel, but shows zero net moment in a unit cell.[1] Contrary to the conventional antiferromagnet, antialigned moments of two different kinds of magnetic ions are exactly compensated by each other. Thus, this is more properly called a compensated half metal (CHM).[2] Since CHM has no net moment, CHM is of extreme interest to spintronics and is anticipated to generate a single-spin superconductor,[3] though no true CHM has yet been established.

After Pickett's prediction,[4] double perovskite (DP) compounds have been investigated as the most promising candidates for CHM. The DP of A_2BB'O$_6$ (A = La or Sr) has a rock-salt structure of transition metals BB'.[5] In spite of many predictions of CHM in DP-related compounds,[4,6–14] no experimental evidence has been observed. The reasons for this are not yet clear, but some seem to result from antisite disorder on B and B' sites.[15] In particular, in systems having 3d ions in both B and B' sites, similar ionic radii often prevent a well-ordered sample from being established, resulting in undermined compensation of magnetic moments.

Ueda *et al.* synthesized artificial LaCrO$_3$/LaFeO$_3$ super-lattices along the [111] direction, proposing a ferromagnetic order with d^3 Cr^{3+} and d^5 Fe^{3+}.[16] Through measurements of the x-ray magnetic circular dichroism in the superlattice sample, Gray *et al.*, who confirmed this trivalent oxidation state, obtained a smaller magnetic moment than a simple estimation of the spin-only magnetic moment and suggested a canted antiferromagnetic order.[17] Very recently, Chakraverty *et al.* synthesized epitaxial La$_2$CrFeO$_6$ films using pulsed laser deposition, obtaining a nearly well-ordered sample with at most 90% order in the B sites.[18] This sample shows the saturated moment of ~ 2 μ_B, implying the antialigned trivalent Cr and Fe state. The moment is consistent with Pickett's theoretical prediction in the well-ordered phase,[3] though the sample shows a small amount of antisite disorder. This implies that the effects of such a small amount of disorder on the net moment are negligible in La$_2$CrFeO$_6$.

From the theoretical point of view, Pickett's calculations within the local spin density approximation (LSDA) indicated the half-metallic ferrimagnet (FI) of La$_2$CrFeO$_6$.[3] Miura and Terakura revisited this compound using the generalized gradient approximation (GGA) and LDA + U.[19] In their GGA calculations, this system had the same moments as Pickett's LSDA, but was insulating. Through LDA + U calculations, they concluded that La$_2$CrFeO$_6$ was insulating and ferromagnetic (FM). However, the experimental observations show that this system is an insulating FI.[18,20]

In this paper, to disentangle this controversy, first we will revisit La$_2$CrFeO$_6$ using LSDA, LDA + U, the modified Becke-Johnson functional,[21] and fixed spin moment (FSM) approaches.[22] Our results confirm the insulating FI La$_2$CrFeO$_6$, consistent with the experimental observations.[18] Second, we will address the electronic and magnetic properties of the as-yet-unsynthesized DP Sr$_2$CrFeO$_6$, mainly using LDA + U, which shows good agreement with the results of the experiment on La$_2$CrFeO$_6$. One of the current authors and Pickett suggested a half semimetallic antiferromagnet in the isovalent and isostructural Sr$_2$CrTO$_6$ (T = Os, Ru).[8] In the previous calculations with LSDA,[8] Sr$_2$CrFeO$_6$ was suggested to be a simple metallic ferrimagnet. However, in our calculations including the Coulomb correlations, DP Sr$_2$CrFeO$_6$ is a precisely compensated half metal, as will be confirmed by FSM studies.

II. STRUCTURE AND CALCULATION

In the cubic DP (space group: $Fm\bar{3}m$, No. 225), the Fe and Cr ions sit on the $4a$ (0,0,0) and $4b$ ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$) sites, respectively. For La$_2$CrFeO$_6$, we used the lattice parameter $a = 7.84$ Å, which was estimated from the experiment.[18] Within LSDA, the internal parameter of O ions, lying on the $24e$ sites (x,0,0), is optimized. Our optimized internal parameter $x = 0.2508$ implies nearly identical oxidation states between the Fe and Cr ions.

For Sr_2CrFeO_6, our preliminary investigations using the SPUDS program indicate that the cubic DP is a stable structure.[23] Besides, considering tetravalent Cr and Fe ions (see below), the tolerance factor is

$$t = \frac{r_A + r_O}{\sqrt{2}\left(\frac{r_B + r_{B'}}{2} + r_O\right)} \approx 1.02,$$

unity for the ideal DP, using the Shannon ionic radius r.[24] Thus, we fully optimized the lattice and internal parameters of the cubic DP in this initial study. Using LSDA, our optimized lattice constant is $a = 7.447$ Å, about 15% smaller volume than La_2CrFeO_6 and Sr_2CrOsO_6.[18,25] The internal parameter $x = 0.2513$ leads to a Cr-O bond length, which is only 0.01 Å shorter than the Fe-O bond length. Here, we neglect such a small distortion as is observed in Sr_2CrOsO_6,[25] since no significant change in the net moment results from this distortion.[8]

Our calculations were carried out with LSDA and LDA + U approaches implemented in two all-electron full-potential codes FPLO and WIEN2K.[26,27] In these LDA + U calculations, two popular double-counting schemes, the so-called around mean field and fully localized limit,[28,29] show similar results for these compounds. The proper values of the on-site Coulomb repulsion U in these systems are unclear, but 3–4 eV for Cr ions[30] and 6 eV for Fe ions have been often used.[31] (The Hund's exchange integral $J = 1$ eV was fixed for all values of U, since results obtained from $U_{eff} = U - J$ were identical with ones from separate U and J inputs.) FSM calculations implemented in FPLO were also carried out to investigate the robustness of our results. In addition, the Becke-Johnson functional modified by Tran and Blaha (the so-called mBJ),[21] implemented in WIEN2K, was used for comparison with our LDA + U results for La_2CrFeO_6. The semilocal functional mBJ is much cheaper than a hybrid functional, but provides reasonable agreement with experiments for transition metal oxides.[21,32]

The Brillouin zone was sampled with a regular mesh containing up to 256 irreducible k points. The structural parameters were optimized until forces were smaller than 1 meV/Å using FPLO. In WIEN2K, the basis size was determined by $R_{mt}K_{max} = 7$ and the APW sphere radii: 2.5 for La, 1.95 for Cr, 1.96 for Fe, and 1.72 for O in La_2CrFeO_6; 2.47 for Sr, 1.84 for Cr, 1.89 for Fe, and 1.64 for O in Sr_2CrFeO_6.

III. REVISITED La_2CrFeO_6

A. Local spin density approximation ground state

To unravel the discrepancies stated in the introduction, we revisit La_2CrFeO_6 using various approaches: LSDA, LDA + U, mBJ, and FSM. All of these calculations give consistent results (see below).

First, we will the address the FSM results within LSDA. The energy vs total moment M plot is given in Fig. 1. We obtained two solutions: FI below $M \approx 3.5 \mu_B$ and FM above $M \approx 4.5 \mu_B$, while both states coexist in the region of $M \approx 3.5$–4.5 μ_B. As M is increased from the precisely compensated state ($M = 0$), the energy decreases monotonically and reaches a minimum at $M = 2 \mu_B$. Below the minimum, the local moment of Cr, $m_{Cr} \approx -2.4 \mu_B$, is nearly unchanged, while

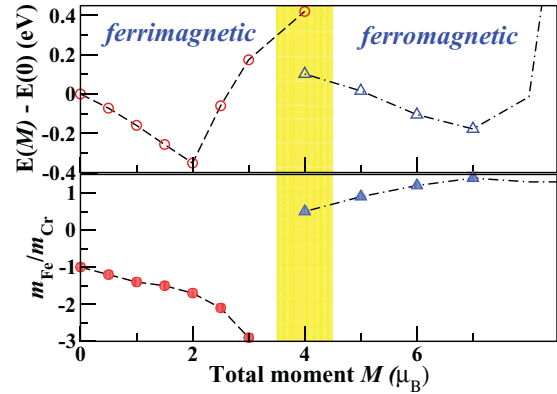FIG. 1. (Color online) LSDA fixed spin moment calculations in La_2CrFeO_6. Top: energy vs total moment M plot. The zero energy $E(0)$ denotes the energy of the exactly compensated state. Bottom: the ratio of local moments m of Fe to Cr. Below $M \sim 3.5 \mu_B$ only FI states can be obtained, while only FM states appear above $M \sim 4.5 \mu_B$. In the shaded regime, both FI and FM states exist. The ground state at $M = 2 \mu_B$ is an insulating FI state, while the others are metallic.

that of Fe increases monotonically. Above the minimum, the magnitude of m_{Cr} decreases and finally becomes almost zero at $M = 4$. The minimum state is insulating, leading to nonanalytic behavior in the FSM curve near the minimum as observed in half metals.[8,33] In the FM regime, the minimum energy occurs at $M \sim 7$. As M is reduced from the minimum, the ratio m_{Fe}/m_{Cr} of the local moments linearly decreases. This FM minimum state has higher energy by 175 meV than the FI minimum state. Thus, our FSM calculations indicate that the ground state is the insulating FI state of $M = 2 \mu_B$, in agreement with our self-consistent calculations (see below).

In LSDA calculations, we obtained both FM and FI states. As mentioned previously, FI is energetically favored over FM. This FM state has the total moment of $M = 7.23 \mu_B$ (3.90 for Fe, 2.74 for Cr, and 0.51 for the six oxygens). In the FI state, the total moment of $M = 2$ is decomposed into local moments of 3.94 for Fe, –2.37 for Cr, and 0.24 for the six oxygens (in units of μ_B). Thus this system has nominally high spin Fe^{3+} ($t_{2g}^{3\uparrow} e_g^{2\uparrow}$) and Cr^{3+} ($t_{2g}^{3\downarrow}$), as is also visible in DOSs given in Fig. 2. Note that the strong p-d hybridization, observable around –6 eV, substantially reduces the Fe moment. The t_{2g}-e_g crystal field splitting of Fe is 2 eV, about 1 eV smaller than the exchange splitting, leading to high spin $S = 5/2$ Fe^{3+}. Both the t_{2g}-e_g crystal field and exchange splittings of Cr are about 2 eV. Compared with the metallic FM state, the antiferromagnetic interactions between Fe and Cr ions lead to gaps in both spin channels, as shown in Fig. 2. So this system becomes a band insulator, consistent with the experiment.[18] Note that the nonmagnetic state has a much higher energy than these two states.

B. Inclusion of correlation effects

Miura and Terakura claimed that the ground state was an insulating FM through LDA + U calculations using a pseudopotential code,[19] in contrast to the experimental observations. We investigated this system using the LDA + U approach, implemented in two all-electron full-potential codes
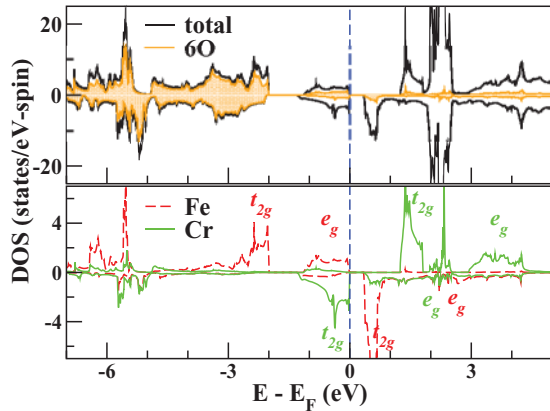
FIG. 2. (Color online) LSDA total and atom-projected densities of states (DOSs) in La$_2$CrFeO$_6$, indicating an insulating FI with gaps of 1.2 and 0.3 eV in the spin-up and spin-down channels. The sharp peaks around 2 eV correspond to La $4f$ bands. Bottom: 3D orbital projected DOSs in Fe and Cr ions. The vertical dashed line denotes the Fermi energy E_F, which is set to zero.

FIG. 4. (Color online) LSDA total and atom-projected DOSs in Sr$_2$CrFeO$_6$, indicating a FI state. The O states lie in the range of –8 to –1.8 eV. The unfilled Cr e_g manifolds in both spin channels exist above 3 eV (not shown here). The density of states $N(E_F)$ at E_F is 5.08 states per eV.

FPLO and WIEN2K.[26,27] We considered the Coulomb correlation of both transition metals in the range of $U = 3$–7 eV. As shown in the calculations of Miura and Terakura, two insulating FM and FI states were obtained. However, in our calculations, the FI with $M = 2$ μ_B is energetically favored over the FM state with $M = 8$ μ_B, regardless of the strength of the on-site Coulomb repulsion U. In particular, at $U = 4$ eV for Cr and 6 eV for Fe, the difference in energy between the states is 86 meV.

To confirm our results, we carried out mBJ calculations, which give the correct magnetic ground state in a parent compound of cuprate CaCuO$_2$.[32] Consistently with our other calculations described above, the FI state has a lower energy by 180 meV than the FM state, indicating that our results are very robust and show good agreement with the experiment.[18] The mBJ total and atom-projected DOSs are given in Fig. 3. Compared with LSDA results shown in Fig. 2, the unoccupied t_{2g} manifolds of Cr in the spin up and Fe in the spin down considerably shift up, while the occupied bands show very
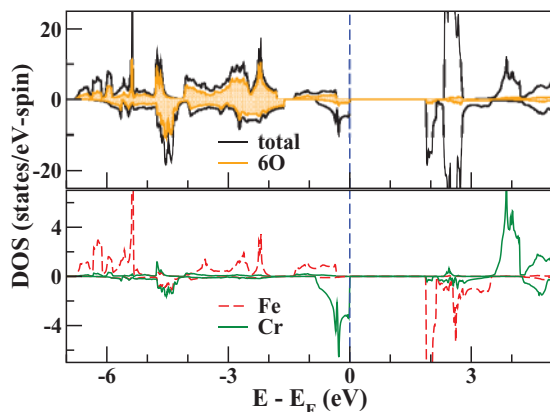

FIG. 3. (Color online) mBJ total and atom-projected DOSs in FI La$_2$CrFeO$_6$, showing a gap of 1.8 eV in the spin-down channel. The unoccupied Cr and Fe t_{2g} manifolds in the spin-up and spin-down channels are at 4 eV and 2 eV, respectively.
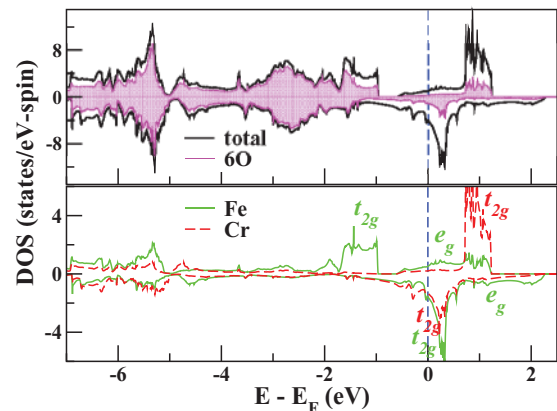
similar features. The local moments are 4.11 for Fe, –2.42 for Cr, and 0.60 for the six oxygens, again resulting in the net moment of 2 (in units of μ_B). The gaps are 2.5 eV and 1.8 eV for the spin-up and spin-down channels, respectively.

IV. ELECTRON STRUCTURE OF Sr$_2$CrFeO$_6$

A. Local spin density approximation electronic structure

The LSDA total and atom-projected DOSs are represented in Fig. 4. In the spin-down channel, the partially filled t_{2g} manifolds of both Cr and Fe lie in the region of –1 to 1 eV, and come into contact with the unfilled Fe e_g manifold. This mixing between Cr and Fe t_{2g} manifolds remains significant even for inclusion of correlation effects (see below), indicating an unusual charge transfer. In the up channel, the completely filled Fe t_{2g} manifold lies in the range of –1.7 to –1 eV, while the center of the unfilled Cr t_{2g} manifold with the width of 0.5 eV is at 1 eV. For Fe ions, the t_{2g}-e_g crystal field splitting of 1.8 eV in the spin up is accidentally equal to the exchange splitting of the t_{2g} manifold. So, some of the Fe e_g bands cross over E_F, undermining the half metallicity. In this state, the Cr moment of –1.32 μ_B is antialigned with those of Fe and the oxygens (1.86 for Fe and 0.21 for 6O), resulting in the total moment 0.75 μ_B. These results indicate formally tetravalent d^2 Cr and d^4 Fe ions of $S = 1$ both in this system, in contrast to trivalent Cr and pentavalent d^3 Os/Ru in Sr$_2$CrTO$_6$. Within LSDA these distinctions between the systems lead to metallic Sr$_2$CrFeO$_6$, but half-semimetallic (i.e., band insulating) Sr$_2$CrTO$_6$. Thus, this requires the inclusion of correlations to Sr$_2$CrFeO$_6$, as is usual in 3d systems. In the next subsection, we will address this issue.

This FI state is energetically favored over the nonmagnetic state by 283 meV, consistent with our FSM calculations (see below). Attempts to obtain a FM state always converged to the FI or nonmagnetic state. Thus, the state of the antialigned moments is very stable.
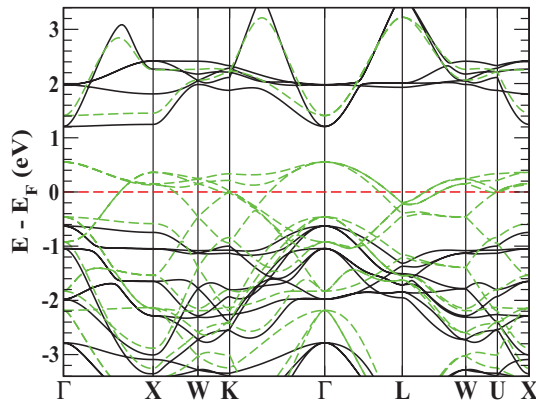
FIG. 5. (Color online) LDA + U band structure for both the spin-up (solid) and spin-down (dashed) channels in Sr_2CrFeO_6, at $U = 4$ eV for Cr and 6 eV for Fe, showing a half metal. The horizontal dashed line denotes E_F, which is set to zero.

B. Correlated electronic structure

In LDA + U calculations, as in La_2CrFeO_6, we used values of U in the range of 3–7 eV for both Cr and Fe ions, showing consistent results. Now, we will focus on results obtained at $U = 4$ eV for Cr and 6 eV for Fe, which have been widely used in perovskite-type oxides.[30,31]

Figure 5 shows an enlarged band structure near E_F, indicating a half metal. The mixture of Cr t_{2g} and e_g manifolds in the spin up and the Fe e_g manifold in the spin down lies in the range from 1 to 3.5 eV. In particular, the Cr t_{2g} around 2 eV is nearly dispersionless. In the spin-up (insulating) channel, the top of the valence bands has mostly O p character, leading to a gap of 1.8 eV between the O p and the Cr e_g bands, as clearly shown in the total and atom-projected DOSs of the top panel of Fig. 6. The Fe t_{2g} manifold in the spin up is completely filled. In the spin-down (conducting) channel, the overlapped t_{2g} manifolds of Fe and Cr are partially filled. In this regime, each character of Cr and Fe is nearly identical to that of the oxygens, indicating strong p-d hybridization. This substantial hybridization is also visible in DOSs of the top panel of Fig. 6. Applying U to both Fe and Cr ions leads to a charge transfer of $0.5e$ (which is measured from the Mullikan charge decomposition in the FPLO method) from the six oxygens to the Fe ion, subsequently enhancing the p-d hybridization. As a result, the moment of Fe remarkably reduces to 0.98 μ_B, but that of the six oxygens increases to 0.42 μ_B. However, the Cr moment remains nearly unchanged, resulting in zero net moment.

We also carried out mBJ calculations in this system. The bottom panel of Fig. 6 shows the corresponding DOSs, reproducing the half metallicity. Compared with LDA + U results, the unfilled Fe e_g manifolds shift toward E_F in both spin channels, leading to decreasing the t_{2g}-e_g crystal field splitting of Fe ions. In the spin down, the partially filled Fe t_{2g} manifold moves upward, while the Cr t_{2g} manifold shifts down. So, the unusual mixing between these t_{2g} manifolds, which is observed in LSDA and LDA + U, is considerably diminished, though some amount of the mixing is still visible. However, the net moment remains zero: 1.80 for Fe, −1.96 for
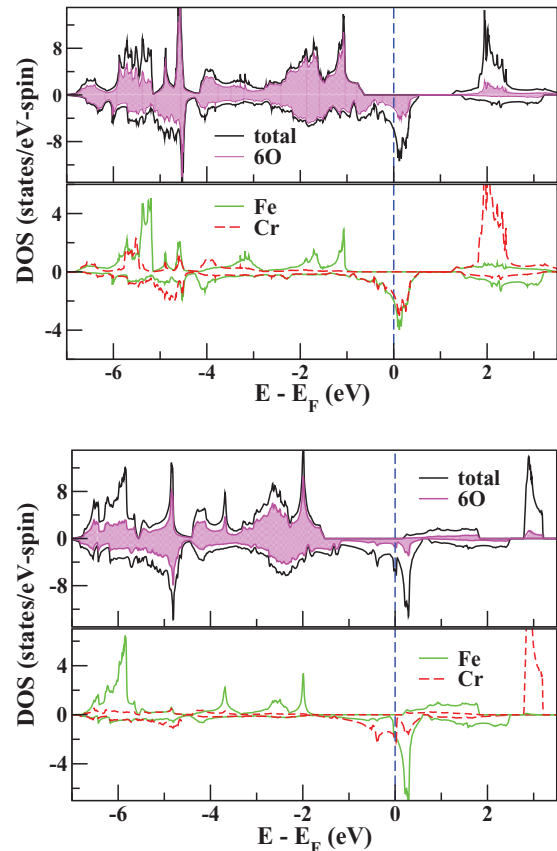

FIG. 6. (Color online) Sr_2CrFeO_6 total and atom-projected DOSs in (top) LDA + U and in (bottom) mBJ. In both results, a gap of $\sim$1.8 eV appears in the spin up. In the spin down, the partially filled t_{2g} manifolds of both Fe and Cr ions cross over E_F. In the spin up, the Fe t_{2g} manifold is fully filled, while the Cr t_{2g} manifold is completely unfilled. This indicates formally Cr^{4+} $t_{2g}^{2\downarrow}$ and Fe^{4+} $t_{2g}^{3\uparrow,1\downarrow}$, though the concept of formal charge is somewhat murky due to strong hybridization.

Cr, and 0.36 for 6O (in units of μ_B). Thus, this system is a precisely compensated half metal.

C. Fixed spin moment studies

To investigate the robustness of this compensated half-metal, we carried out FSM calculations.[22] The change in energy vs total moment M plot is given in Fig. 7. In LSDA, we obtained two curves. In the range of $M = 0$ to 2.5 μ_B FI solutions are obtained, while FM solutions are obtained above 2.7 μ_B. The FI state with $M = 0.75$ μ_B is the ground state, about 50 meV lower in energy than CHM. At $M = 0$, the nonmagnetic state has 230 meV higher energy than CHM. So, a state having antialigned moments of Cr and Fe ions is energetically favored.

The inset of Fig. 7 shows FSM results for FM states in LDA + U. Note that the CHM state with $M = 0$, which is set to the zero energy, has lowest energy. Contrary to the LSDA results, FI states could be obtained only near $M \approx 0$ (not shown here). Interestingly, a plateau appears in the range of $M = 1$ to 2 μ_B. Our self-consistent calculations also produce a FM state
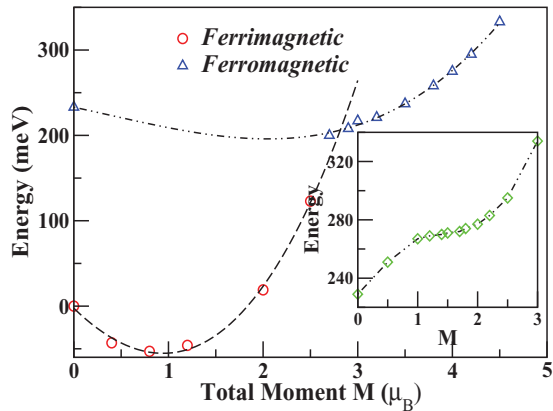
FIG. 7. (Color online) Fixed spin moment (FSM) calculations of LSDA in Sr_2CrFeO_6. The symbols of circles and triangles indicate FI and FM states, respectively. The zero energy is set to the energy of an exactly compensated FI state with $M = 0$. Inset: FSM of LDA + U at $U = 4$ and 6 eV for Cr and Fe ions, respectively. This shows a change in energy for FM, except for nonmagnetic state at $M = 0$. A plateau appears in the regime of $M \approx 1$ to 2 μ_B. The zero energy denotes CHM, which is the ground state in the LDA + U calculations.

having $M \approx 2$ in LDA + U. This implies that a metastable state may appear in the regime of a plateau.

V. DISCUSSION AND SUMMARY

Figure 8 displays the schematic atom-projected DOSs of both transition metals in La_2CrFeO_6, Sr_2CrFeO_6, and Sr_2CrRuO_6, indicating two interesting aspects. First, Fe ions are in the d^5 $S = 5/2$ high spin state in La_2CrFeO_6, but in the d^4 $S = 1$ low spin state in Sr_2CrFeO_6. To uncover the origin of the transition of the Fe spin states when replacing La with Sr, we carried out calculations of Sr_2CrFeO_6 with the same structure as La_2CrFeO_6. Our results show that Sr_2CrFeO_6 has a similar electronic structure to La_2CrFeO_6, with the only difference being the band filling, resulting in a simple ferrimagnetic metal with a d^4 $S = 2$ high spin Fe ion. This indicates that the 15% volume in Sr_2CrFeO_6 reduction leads to an increase in the crystal field splitting, and subsequently the transition. Second, Sr_2CrFeO_6 is half metallic, while an
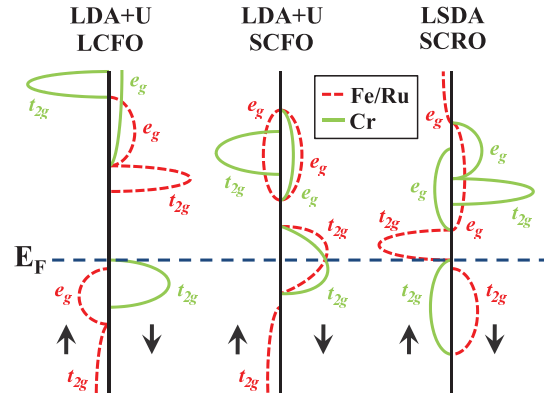

FIG. 8. (Color online) Simplified Cr and Fe atom-projected DOSs of La_2CrFeO_6 and Sr_2CrFeO_6 of LDA + U, compared with Cr- and Ru-projected DOSs of LSDA Sr_2CrRuO_6, which has been predicted to be a compensated half semimetal.[13] In these systems, Cr ions follow the first Hund's rule.

isovalent and isostructural Sr_2CrRuO_6 is semimetallic. CHM Sr_2CrFeO_6 remains unchanged even for our calculations with the same structure as Sr_2CrRuO_6. Thus, this distinction results from chemical differences between Fe and Ru ions rather than differences in the crystal structure.

In summary, we revisited a well-ordered DP La_2CrFeO_6, which shows noticeable discrepancies between the predictions of existing models and the experimental results, through various first-principles approaches implemented in two all-electron full-potential codes. Our calculations show good agreements with the experiment,[18] indicating an insulating ferrimagnet with $M = 2$ μ_B. Furthermore, we investigated the unsynthesized DP Sr_2CrFeO_6. Our LSDA + U results suggest a compensated half-metallic Sr_2CrFeO_6 with nominal Cr^{4+} ($t_{2g}^{2\downarrow}$) and Fe^{4+} ($t_{2g}^{3\uparrow,1\downarrow}$), which is confirmed by the FSM calculations. This CHM Sr_2CrFeO_6 is expected to be synthesized by the recently developed method that is used to synthesize La_2CrFeO_6 and Sr_2CrOsO_6.[18,25]

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