Evaluation of Half-metallic Antiferromagnetism in $A_2$CrFeO$_6$ ($A$=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 $S=\frac{3}{2}$ Cr$^{3+}$ and $S=\frac{5}{2}$ Fe$^{3+}$ ions, using the local spin density approximation (LSDA), a correlated band theory LDA+U, and a semilocal functional 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$_6$.

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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. 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). Since CHM has no net moment, CHM is of extreme interest to spintronics and is anticipated to generate a single spin superconductor though no true CHM has yet been established.

After Pickett’s prediction double perovskite (DP) compounds have been investigated as the most promising candidates for CHM. The DP of $A_2$BB’O$_6$ ($A=$ La or Sr) has a rock-salt structure of transition metals BB’$^{4+}$. In spite of many predictions of CHM in DP-related compounds, 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. In particular, in systems having 3$d$ 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$_3$ superlattices along the [111] direction, proposing a ferromagnetic order with $d^{3}$ Cr$^{3+}$ and $d^{5}$ Fe$^{3+}$. 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. 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. This sample shows the saturated moment of $\sim 2\mu_H$, implying the antialigned trivalent Cr and Fe state. The moment is consistent with Pickett’s theoretical prediction in the well-ordered phase 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$_6$. Miura and Terakura revisited this compound using the generalized gradient approximation (GGA) and LDA+U. 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.

In this paper, to disentangle this controversy, first we will revisit La$_2$CrFeO$_6$ using LSDA, LDA+U, the modified Becke-Johnson functional and fixed spin moment (FSM) approach. Our results confirm the insulating FI La$_2$CrFeO$_6$, consistent with the experimental observations. 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$_2$Cr$_3$O$_6$ ($T$=Os, Ru). In the previous calculations with LSDA, Sr$_2$Cr$_3$O$_6$ was suggested to be a simple metallic ferrimagnet. However, in our calculations including the Coulomb correlations, DP Sr$_2$Cr$_3$O$_6$ is a precisely compensated half-metal, as will be confirmed by FSM studies.

II. STRUCTURE AND CALCULATION

In the cubic DP (space group: $Fmar{3}m$, 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. Within LSDA, the internal parameter of O ions, lying on the $24e$ sites ($x$,$x$,$x$), is optimized. Our optimized internal parameter $x = 0.2508$ implies nearly identical oxidation states between the Fe and Cr ions.

For Sr$_2$CrFeO$_6$, our preliminary investigations using the Spuds program indicate that the cubic DP is a stable structure. Besides, considering tetravalent Cr and Fe ions (see below), the tolerance factor is

$$t = \frac{r_A + r_O}{\sqrt{2(r_B + r_M + r_O)}} \approx 1.02,$$

unity for the ideal DP, using the Shannon ionic radius $r$. 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$_2$CrFeO$_6$ and Sr$_2$CrO$_6$. 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$_2$CrO$_6$ since no significant change in the net moment results from this distortion.

Our calculations were carried out with LSDA and LDA+U approaches implemented in two all-electron full-potential codes FPLO and WIEN2k. In these LDA+U calculations, two popular double-counting schemes, the so-called around mean field and fully localized limit, 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 and 6 eV for Fe ions have been often used. (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.)

FIG. 1: (Color online) LSDA fixed spin moment calculations in La$_2$CrFeO$_6$. 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 $M \approx 3.5 \mu_B$ only FI states can be obtained, while only FM states appear above $M \approx 4.5 \mu_B$. 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.

III. REVISITED La$_2$CrFeO$_6$

A. LSDA ground state

To unravel the discrepancies stated in the introduction, we revisit La$_2$CrFeO$_6$ 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. I. 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 $M \approx 3.5-4.5 \mu_B$. 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 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. 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 $\mu_B$). Thus this system has nominally high spin Fe$^{3+}$ ($t_{2g}^{3}e_{g}^{2}$) and Cr$^{3+}$ ($t_{2g}^{3}$) 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 $e_g$ for the exchange splitting, leading to high spin $S=\frac{5}{2}$ 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. Note that the nonmagnetic state has a much higher energy than these two states.

![DOS](image1.png)

**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 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. 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 down channels are at 4 eV and 2 eV, respectively.

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 in contrast to the experimental observations. We investigated this system using the LDA+U approach, implemented in two all-electron full-potential codes FPLO and WIEN2k. 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 $M=2 \mu_B$ is energetically favored over the FM state with $M=8 \mu_B$, 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$_2$. 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. The mBJ total and atom-projected DOSs are given...
shown here). The density of states 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.

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 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 $\mu_B$). The gaps are 2.5 eV and 1.8 eV for the spin up and down channels, respectively.

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

A. LSDA 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-metallic. In this state, the Cr moment of –1.32 $\mu_B$ is antialigned with those of Fe and the oxygens (1.86 for Fe and 0.21 for O), resulting in the total moment 0.75 $\mu_B$. These results indicate formally tetravalent $d^3$ Cr and $d^4$ Fe ions of $S=1$ both in this system, in contrast to trivalent Cr and pentavalent $d^5$ 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 non-magnetic 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.

B. Correlated electronic structure

In LDA+U calculations, as in La$_2$CrFeO$_6$, 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 Mulliken 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 $\mu_B$, but that of the six oxygens increases to 0.42 $\mu_B$. 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 Cr, and 0.36 for 6O (in units of $\mu_B$). 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. 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 $\mu_B$ FI solutions are obtained, while FM solutions are obtained above 2.7 $\mu_B$. The FI state with $M=0.75$ $\mu_B$ 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 $\mu_B$. Our self-consistent calculations also produce a FM state having $M \approx 2$ in LDA+U. This implies that a meta-stable 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$_2$CrFeO$_6$, Sr$_2$CrFeO$_6$, and Sr$_2$CrRuO$_6$, indicating two interesting aspects. First, Fe ions are in the $d^6$ $S=\frac{5}{2}$ high spin state in La$_2$CrFeO$_6$, but in the $d^4$ $S=1$ low spin state in Sr$_2$CrFeO$_6$. To uncover the origin of the transition of the Fe spin states when replacing La with Sr, we carried out calculations of Sr$_2$CrFeO$_6$ with the same structure as La$_2$CrFeO$_6$. Our results show that Sr$_2$CrFeO$_6$ has a similar electronic structure to La$_2$CrFeO$_6$, 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$_2$CrFeO$_6$ reduction leads to an increase in the crystal field splitting, and subsequently the transition. Second, Sr$_2$CrFeO$_6$ is half-metallic, while an isovalent and isostructural Sr$_2$CrRuO$_6$ is semimetallic. CHM Sr$_2$CrFeO$_6$ remains unchanged even for our calculations with the same structure as Sr$_2$CrRuO$_6$. 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$_2$CrFeO$_6$, 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 indicating an insulating ferrimagnet with $M=2$ $\mu_B$. Furthermore, we investigated the unsynthesized DP Sr$_2$CrFeO$_6$. Our LSDA+U results suggest a compensated half-metallic Sr$_2$CrFeO$_6$ with nominal Cr$^{4+}$ ($t_{2g}^2$) and Fe$^{3+}$ ($t_{2g}^3$), which is confirmed by the FSM calculations. This CHM Sr$_2$CrFeO$_6$ is expected to be synthesized by the recently developed method that is used to synthesize La$_2$CrFeO$_6$ and Sr$_2$CrOsO$_6$.

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