

# Electronic structure of the ferromagnetic double-perovskites $\text{Sr}_2\text{CrReO}_6$ , $\text{Sr}_2\text{CrWO}_6$ , and $\text{Ba}_2\text{FeReO}_6$

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**Abstract.** We have studied the electronic structure of the ferromagnetic double perovskites  $\text{Sr}_2\text{CrReO}_6$ ,  $\text{Sr}_2\text{CrWO}_6$  and  $\text{Ba}_2\text{FeReO}_6$  by means of a full-potential linear muffin-tin orbital density-functional method. Our scalar-relativistic calculations predict these compounds to be half-metallic with a total magnetic moment of 1, 2, and 3  $\mu_B$  respectively. However, when the spin-orbit coupling is included, the 5d transition Re and W ions exhibit substantial unquenched orbital magnetic moments, resulting in a significant increase of the total magnetic moment. The half-metallic gap turns into a pseudo-gap in  $\text{Sr}_2\text{CrReO}_6$  and  $\text{Ba}_2\text{FeReO}_6$  when the spin-orbit coupling is included whereas  $\text{Sr}_2\text{CrWO}_6$  remains half-metallic even with spin-orbit coupling. The calculated spin and orbital magnetic moments agrees well with the recent experimental XMCD measurements.

## 1. Introduction

Perovskite compounds have recently attracted a great deal of interest in basic and applied research due to their extraordinary structural, magnetic and electronic properties. In recent years we have witnessed an increased interest in the study of transition metal oxides with an ordered double perovskite structure  $\text{A}_2\text{BB}'\text{O}_6$  (where A=alkaline earth or rare earth and BB' are heterovalent transition metals such as B=Fe,Cr,Mn,Co,Ni; B'=Mo,Re,W). Novel and attractive properties that can be useful in future spintronic device applications have been demonstrated, such as the large tunneling type magnetoresistance observed at room temperature, as well as the low field magnetoresistance found in  $\text{Sr}_2\text{FeMoO}_6$  [1]. The physical origin of the magnetoresistance in  $\text{Sr}_2\text{FeMoO}_6$  and in the mixed valent manganese oxides is half-metallicity, i.e., the material is an insulator in one of the spin channels, but a metal in the other. This leads to a complete spin polarization at the Fermi level, which immediately suggests their application as a source of spin polarized charge carriers in spintronic devices. Ferromagnetism with a  $T_c$  up to 458 K has been observed not only in  $\text{Sr}_2\text{FeMoO}_6$  but also in ceramic and thin films of  $\text{Sr}_2\text{CrWO}_6$ [2]. The double perovskite with the highest  $T_c$  known so far is  $\text{Sr}_2\text{CrReO}_6$  with  $T_c=635$  K[3, 4]. Several other Fe-based ordered double perovskites  $\text{A}_2\text{FeBO}_6$  (A=Ca,Ba,Sr; B=Mo,Re) have also been reported to have half-metallic nature and high  $T_c$  [5, 6, 7]. One exception is  $\text{Ca}_2\text{FeReO}_6$  which undergoes a metal-insulator transition [8].

**Table 1.** Calculated spin and orbital magnetic moments of the non-magnetic transition metals. The experimental values for  $\text{Sr}_2\text{CrReO}_6$  and  $\text{Sr}_2\text{CrWO}_6$  are taken from Ref.15 and 16.

Compound	Theory		Expt.	
	$\mu_s$	$\mu_l$	$\mu_s$	$\mu_l$
$\text{Sr}_2\text{CrReO}_6$	-0.85	0.18	-0.68	0.25
$\text{Sr}_2\text{CrWO}_6$	-0.31	0.10	$-0.33\pm 0.02$	$0.12\pm 0.02$
$\text{Ba}_2\text{FeReO}_6$	-0.65	0.19	-	-

Several first-principles density functional calculations explaining the electronic and magnetic properties of  $\text{Sr}_2\text{CrReO}_6$ ,  $\text{Sr}_2\text{CrWO}_6$  and  $\text{Ba}_2\text{FeReO}_6$  are available[9, 10, 11]. However, only very limited studies have so far been made regarding the effect of spin-orbit coupling on the half-metallic gap and the orbital magnetic moments at the non-magnetic B' site. Hence, in the present work efforts have been made to study the effects of spin-orbit coupling on the electronic structure and to calculate the orbital magnetic moments at the  $5d$  transition metal site. The rest of the paper is organized as follows. The computational details are given in Section II and the results are summarized in Section III.

## 2. Computational details

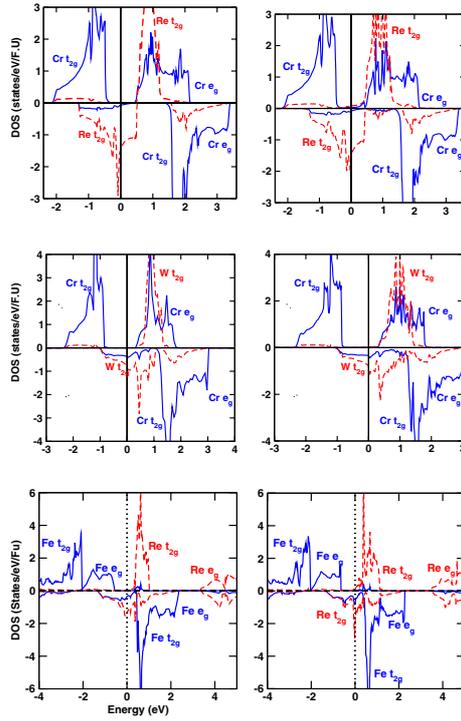
Our calculations are based on density-functional theory within the generalized gradient approximation (GGA) for the exchange-correlation potential [12]. We employ the full-potential linear muffin-tin orbital method (FP-LMTO), which has been described in detail elsewhere[13]. Spin-orbit coupling was included in our calculations. The spherical-harmonic expansion of the potential was performed up to  $l_{max} = 6$ , and we used a double basis so that each orbital is described using two different kinetic energies in the interstitial region. Furthermore, we included several pseudo-core orbitals in order to further increase accuracy. Thus, the basis set consisted of the Ba ( $5s$   $6s$   $5p$   $6p$   $5d$ ), Fe ( $4s$   $3p$   $4p$   $3d$ ), Sr ( $4s$   $5s$   $4p$   $5p$   $4d$ ), Cr ( $4s$   $3p$   $4p$   $3d$ ), Re ( $6s$   $5p$   $6p$   $5d$ ), and O ( $2s$   $2p$ ) LMTOs. For all three compounds, we performed our calculations assuming the experimentally determined structures [3, 2, 5].

## 3. Results

The calculated density of states (DOS) for  $\text{Sr}_2\text{CrReO}_6$ ,  $\text{Sr}_2\text{CrWO}_6$  and  $\text{Ba}_2\text{FeReO}_6$  are given in figure 1. From the DOS in the left column one can clearly see that all three compounds are half-metallic in the absence of spin-orbit coupling.

The gap in the spin-up channel is around 0.7 eV for  $\text{Sr}_2\text{CrReO}_6$  and around 0.85 eV for  $\text{Sr}_2\text{CrWO}_6$ . In  $\text{Sr}_2\text{CrReO}_6$  and  $\text{Sr}_2\text{CrWO}_6$  the Fermi level falls just where the Cr  $3d$  spin-up band is split by the crystal field, whereas in the spin down channel there is a considerable hybridization of Cr  $3d$  with Re  $5d$  and W  $5d$  states at the Fermi level. This results in a total spin-magnetic moment of  $1 \mu_B$  for  $\text{Sr}_2\text{CrReO}_6$  and  $2 \mu_B$  for  $\text{Sr}_2\text{CrWO}_6$ . In contrast, for  $\text{Ba}_2\text{FeReO}_6$ , one can see that the half-metallic gap of 0.7 eV which lies inbetween the Fe- $e_g$  and Re- $t_{2g}$  states in the spin-up channel. For this compound, we get a total spin magnetic moment of  $3 \mu_B$ , which is consistent with the expected half-metallic nature of this compound.

The calculated density of states including the spin-orbit coupling is shown in the rightmost column of figure 1. It can be clearly seen that in  $\text{Sr}_2\text{CrReO}_6$ , when spin-orbit coupling is included, the band gap disappears and turns into a pseudo-gap with a low but finite DOS. As a first hint as to why the gap disappears, we note that in Re metal, the spin-orbit parameter



**Figure 1.** Orbital-resolved density of states for  $\text{Sr}_2\text{CrReO}_6$ ,  $\text{Sr}_2\text{CrWO}_6$  and  $\text{Ba}_2\text{FeReO}_6$  GGA calculation, without spin-orbit coupling (left panel), and with spin-orbit coupling (right panel). The Fermi level is at zero.

$\zeta(r)$  of the  $t_{2g}$  states in the spin-orbit Hamiltonian  $\hat{H}_{SO} = \zeta(r) \hat{\mathbf{I}} \cdot \hat{\mathbf{s}}$  is around 0.4 eV, a number that decreases to approximately 0.3 eV in the double perovskite due to covalency.[14] Thus, the half-metallic gap and the spin-orbit splitting are of the same order, which makes it plausible that the spin-orbit splitting is capable of washing away the gap. In  $\text{Sr}_2\text{CrWO}_6$  the half-metallic gap is preserved even with spin-orbit coupling in contrast to  $\text{Sr}_2\text{CrReO}_6$ . The main difference between  $\text{Sr}_2\text{CrWO}_6$  and  $\text{Sr}_2\text{CrReO}_6$  is that W has one 5d electron less than Re, causing the W  $t_{2g}$  states to shift upwards in energy, away from the Fermi level. As a result, the hybridization at the gap becomes less pronounced, and the gap is preserved. In the case of  $\text{Ba}_2\text{FeReO}_6$  a situation similar to that  $\text{Sr}_2\text{CrReO}_6$  is observed, i.e., the half-metallic gap and spin-orbit splitting are of the same order, giving rise to a pseudo-gap and destruction of the half-metallicity for this system.

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### References

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- [1] K. I. Kobayashi, T. Kimura, H. Sawada, K. Terakura and Y. Tokura 1998 *Nature (London)* **395**, 677.
- [2] J. B. Philipp, P. Majewski, L. Alff, A. Erb, R. Gross, T. Graf, M. S. Brandt, J. Simon, T. Walther, W. Mader D. Topwal, and D. D. Sarma 2003 *Phys. Rev. B* **68**, 144431.
- [3] H. Kato, T. Okuda, Y. Okimoto, Y. Tomioka, Y. Takenoya, A. Ohkubo, M. Kawasaki and Y. Tokura 2002 *Appl. Phys. Lett.* **81**, 328.
- [4] H. Asano, N. Kozuka, A. Tsuzuki, and M. Matsui 2004 *Appl. Phys. Lett.* **85**, 263.

- [5] J. M. De Teresa, D. Serrate, J. Blasco, M. R. Ibarra, and L. Morellon 2004 *Phys. Rev. B* **69**, 144401.
- [6] C. Ritter, M. R. Ibarra, L. Morellon, J. Blasco, J. Garcia, and J. M. De Teresa 2000 *J. Phys. C* **12**, 8295.
- [7] J. A. Alonso, M. T. Casais, M. J. Martinez-Lope, J. L. Martinez, P. Velasco, A. Munoz, and M. T. Fernandez-Diaz 2000 *Chem. Mater.* **12**, 161.
- [8] H. Kato, T. Okuda, Y. Okimoto, Y. Tomioka, K. Oikawa, T. Kamiyama, and Y. Tokura 2002 *Phys. Rev. B* **65**, 144404.
- [9] G. Vaitheeswaran, V. Kanchana, and A. Delin 2005 *Appl. Phys. Lett.* **85**, 032513.
- [10] H.T. Jeng, and G. Y. Guo 2003 *Phys. Rev. B* **67**, 094438.
- [11] H. Wu 2001 *Phys. Rev. B* **64**,125126.
- [12] J. P. Perdew, K. Burke, and M. Ernzerhof 1996 *Phys. Rev. Lett.* **77**, 3865.
- [13] J. M. Wills, O. Eriksson, M. Alouani and O. L. Price in *Electronic Structure and Physical Properties of Solids*, edited by H. Dreyssé (Springer, Berlin 2000).
- [14] O. K. Andersen (Private Communications).
- [15] P. Majewski *et al.* 2005 *Appl. Phys. Lett.* **87**, 202503
- [16] P. Majewski, S. Geprägs, A. Boger, M. Opel, A. Erb, R. Gross, G. Vaitheeswaran, V. Kanchana, A. Delin, F. Wilhelm, A. Rogalev, L. Alff 2005 *Phys. Rev. B* **72**, 132402