A Letters Journal Exploring the Frontiers of Physics

November 2008

EPL, **84** (2008) 47005
doi: 10.1209/0295-5075/84/47005

www.epljournal.org

Ab initio calculated X-ray magnetic circular dichroism of Sr_2CrReO_6

G. Vaitheeswaran[1(a)], V. Kanchana[1], M. Alouani[2] and A. Delin[1]

[1] *Department of Materials Science and Engineering, Royal Institute of Technology (KTH)*
Brinellvägen 23, 10044 Stockholm, Sweden, EU
[2] *Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504 CNRS-ULP*
23 rue du Loess, 67034 Strasbourg Cedex, France, EU

received 24 June 2008; accepted in final form 3 October 2008

PACS `71.70.Ej` – Spin-orbit coupling, Zeeman and Stark splitting, Jahn-Teller effect
PACS `71.15.Ap` – Basis sets (LCAO, plane-wave, APW, etc.) and related methodology (scattering methods, ASA, linearized methods, etc.)
PACS `77.84.Bw` – Elements, oxides, nitrides, borides, carbides, chalcogenides, etc.

Abstract – *Ab initio* calculated X-ray absorption and X-ray magnetic circular dichroism (XMCD) spectra at the Cr and Re $L_{2,3}$ edges for the double perovskite Sr_2CrReO_6 are compared with experiment. The main features of the experimental spectra are reproduced by the calculations, however, the amplitudes of several structures are significantly over- or underestimated. The calculated spin and orbital magnetic moments for Cr and Re agree with those obtained by means of XMCD sum rules, except for the Cr orbital moment, illustrating that numerical uncertainties can be large for small moments. It is also argued that the Re moments are induced and not intrinsic.

Transition metal oxides have emerged as a class of interesting materials with potential use in spintronic devices [1]. A few of these oxides are so-called half-metals, *i.e.*, metallic in one spin direction and insulating in the other. This particular electronic structure would in principle lead to infinite tunneling magnetoresistance, which has spurred intense research in the area. The most famous member of this class of materials is the double perovskite Sr_2FeMoO_6 [2] (SFMO for short).

Perfect half-metallicity can of course only exist at low temperatures and only for perfectly ordered materials. It can also be affected by electron-electron correlation and spin-orbit coupling [3] (SOC). Thus, in the search for useful new materials, it is not critical to search for true half-metals. Materials with a high spin polarization at the Fermi level combined with a high Curie temperature and other aspects, such as ease of fabrication, stability against corrosion, low coercive field and multifunctionality, are more interesting for applications. In particular, research has lately focussed on double perovskites with higher Curie temperature T_C than that of SFMO which has a T_C of 418 K [2,4].

In this study, we concentrate on the double perovskite Sr_2CrReO_6 (SCRO), which has a high T_C of 635 K [5], and is very close to being a half-metal [6]. We have calculated, from first principles, the X-ray absorption spectra (XAS) and the X-ray magnetic circular dichroism (XMCD) spectra at the $L_{2,3}$ edges for both Cr and Re. The explicit calculation of the spectra is interesting since it provides a more direct way of comparing experimental results with theoretical models of the electronic structure, and in addition constitutes a sensitive test of our theoretical method. The spin and orbital moments are obtained directly from the self-consistent calculation, and in addition from the calculated spectra using the XMCD sum rules [7]. This procedure allows us to evaluate how well the sum rules work in different cases.

The present spin-polarized density-functional calculations were performed using an all-electron full-potential linear muffin-tin orbital method (FP-LMTO), which has been described in detail elsewhere [8]. We performed the calculations in the experimentally reported tetragonal structure with space group symmetry $I4/mmm$ [5] and used the same sphere radii as in our earlier work [6]. The spherical-harmonic expansion of the potential was performed up to $l_{max} = 6$, and we used a double basis so

---

[(a)] E-mail: `vaithee@kth.se`

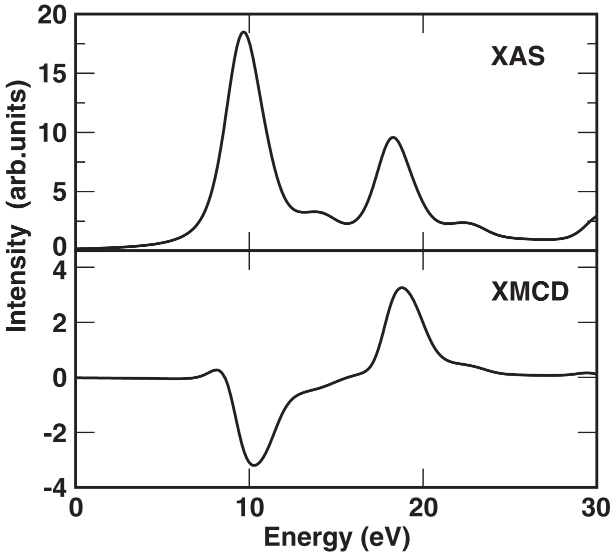

Fig. 1: Calculated XAS and XMCD spectra at the Cr $L_{2,3}$ edges.

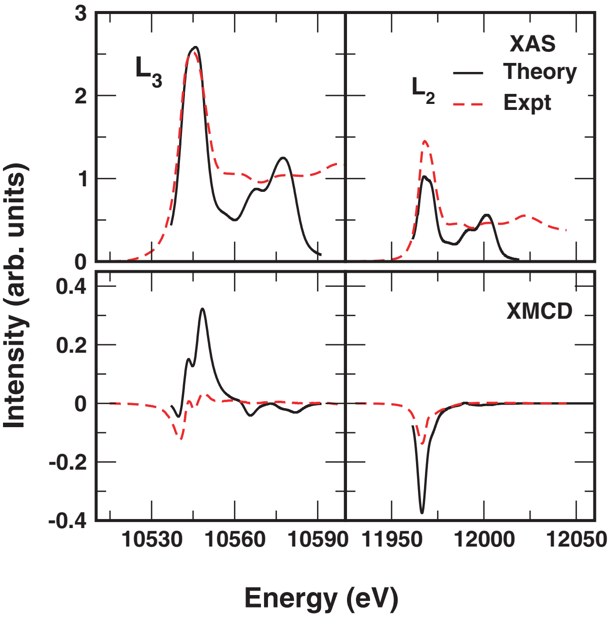

Fig. 2: (Color online) Calculated XAS and XMCD spectra of the Re L_2 and L_3 edges (full lines) as compared with the experimental spectra from ref. [13] (dashed lines).

that each orbital is described using two different kinetic energies in the interstitial region. The basis consists of Sr ($4s$ $5s$ $4p$ $5p$ $4d$), Cr ($4s$ $3p$ $4p$ $3d$), Re ($6s$ $5p$ $6p$ $5d$), and O ($2s$ $2p$), LMTOs. We used LSDA for the calculation of the XAS and XMCD spectra with 78 $\mathbf{k}$ points in the irreducible Brillouin zone. The SOC was included in all calculations —without it, no XMCD signal would emerge. We have used the LSDA to calculate the XAS and XMCD spectra because the calculated magnetic moments are in much better agreement with the experiment results than the GGA values. In addition, LSDA calculations are somewhat less time consuming when compared to GGA calculations because the accurate calculation of gradient terms need higher numerical precision and denser meshes.

Details on how the calculation of XAS and XMCD spectra was implemented in the FP-LMTO method can be found in ref. [9]. The electron-hole interaction was not taken into account in our calculation. We convoluted our calculated spectra using a Lorentzian followed by a Gaussian, both of full-width at half-maximum (FWHM) of 0.25 eV for Cr and 0.5 eV for Re. The Gaussian and Lorentzian broadenings represent, respectively, the experimental resolution and the width of the core hole. We used 6.3 d holes for Cr and 5.3 holes for Re in the sum rule calculation of the moments. The number of d holes has been determined by integrating the unoccupied atom-resolved d DOS up to an energy cutoff of 10 eV similar to the recent SFMO calculation [10].

The main results of this letter are the calculated $L_{2,3}$ edge XAS and XMCD spectra for SCRO, presented in figs. 1 (Cr) and 2 (Re), along with the calculated spin and orbital moments in table 1. Starting with the Cr results, our calculated spectra exhibit a clear XMCD signal with a simple structure —a negative peak at the L_2 edge followed by a positive peak at the L_3 edge. We find a Cr spin moment of about $2\,\mu_B$, and a nearly quenched orbital moment, see table 1. The spin and orbital moments are anti-parallel, which is consistent with Hund's rule for $3d$ shells that are less than half-filled. A similar quenched orbital magnetic moment for Cr atom has been recently reported for the half-metallic ferromagnet CrO_2 [11]. In table 1, the moments have been calculated in two ways —from the self-consistent calculation and by applying the XMCD sum rules. Both methods yield identical spin moments for Cr, whereas the sum-rule–calculated orbital moment is twice as large as the self-consistent moment. This discrepancy between the direct calculation and the sum rule could be also in part explained by the fact that the sum rules are only derived in the electric-dipole approximation [12]. Neither experimental spectra nor measured magnetic moments have been published so far to which we can compare our Cr results.

In contrast, experimental XAS and XMCD spectra for Re in SCRO have been published [13] and are compared in fig. 2 to our calculated Re spectra. We have normalized the amplitudes of the spectra by equating the experimental and theoretical amplitudes for the L_3 XAS main peak. We notice that the Re spectra are more complex than the Cr ones. Our calculations reproduce the main structures of the XAS spectra, but the L_2 amplitude is underestimated. Also, the calculations give two additional, weaker, peaks which appear smeared out in the experimental spectra. The calculated amplitudes are significantly higher than the experimental ones at both L edges. The experimental L_3 XMCD spectrum starts with a negative peak followed by two smaller positive peaks. Our calculated spectrum reproduces these peaks but

Table 1: Spin (m_s) and orbital (m_l) d magnetic moments in μ_B/atom for SCRO obtained from the self-consistent (SC) calculation and from the sum rules (SR) along with the experimental values taken from ref. [13].

	Spin			Orbital			m_l/m_s		
	SC	SR	Expt.	SC	SR	Expt.	SC	SR	Expt.
Cr	2.02	2.02	–	−0.029	−0.059	–	−0.014	−0.029	–
Re	−0.69	−0.78	−0.68	0.17	0.20	0.25	−0.25	−0.26	−0.37

the amplitudes are different from the experimental ones. The L_2 edge XMCD spectrum exhibits just one peak, well reproduced in our calculations although also here, the calculated amplitude is significantly larger than the experimental one. This discrepancy is most probably due to the neglect of the core-hole effects. Another source of discrepancy is the anti-site disorder in the experimental sample. The disorder is not treated within our calculation and it may contribute significantly to the XMCD spectral shape. A similar discrepancy has been observed in our earlier work on Ni-based Huesler alloys [14] and in double perovskite SFMO [10]. On the other hand, Cr is a $3d$ metal and thus the $3d$ band is rather narrow and correlation effects can be expected to be important. However, many properties of $3d$ metals are still astonishingly well described using LSDA or GGA functionals, due to the large metallic screening. Correlation effects will definitely play a role in the spectra as the exchange splitting of the d states increases. However, SCRO is metallic and hence correlation effects will be screened out to a large extent.

Our self-consistently calculated Re spin moment is very close to the experimental value (-0.69 and $-0.68\,\mu_B$, respectively), whereas the sum-rule–calculated spin moment is 13% larger. The calculated Re orbital moment is significantly smaller than the experimental one, 0.17 and $0.25\,\mu_B$, respectively. As for the Re spin moment, the sum rule value is a bit larger than the the self-consistent calculation. The magnitudes of the sum-rule–calculated spin and orbital moments depend on the number of d holes. In order to present a result independent of this number, we added the m_l/m_s ratio to table 1. Notice that this ratio is almost identical for the self-consistent and sum-rule–calculated moments (0.25 and 0.26, respectively) and that both these theoretical values are significantly lower than the experimental result of 0.37. The underestimated m_l/m_s ratio might point toward the possible importance of orbital polarization, which is a way of including Hunds second rule, *i.e.* maximization of the orbital moment under the condition of maximal spin moment. Thus, we expect that the inclusion of orbital polarization will, in general, lead to an increase of the calculated moment. For Fe, Co and Ni, orbital polarization results in an increase of the calculated orbital moments, and for delta-Pu it increases the orbital moment from 2 to $3\,\mu_B$ [15]. However, the orbital polarization seems not to improve significantly the XMCD spectra [16].

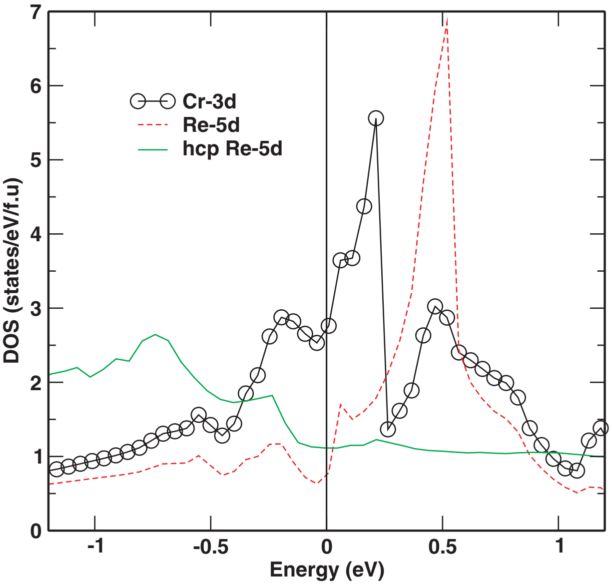

Fig. 3: (Color online) Orbital-resolved Re $5d$ density of states (DOS) at the vicinity of the Fermi level from nonmagnetic calculations of SCRO (red dashed line) and Re hcp (green continuous line) at the experimental lattice constants in fu (formula unit). Also plotted are the SCRO Cr $3d$ states, in black (continuous line with circles).

An interesting question is whether the rather large Re moment observed is purely induced through hybridization with the spin-polarized Cr states, or if it can be regarded as intrinsic in this compound [13]. In a simple picture of spin polarization, one compares the gains and losses of the kinetic and exchange energies. Spin polarization lowers the exchange energy, but it is payed for by increased kinetic energy. When the bands have low enough dispersion at the Fermi level, *i.e.*, the density of states is high enough, the balance rules in favor of spin polarization. This idea is expressed in quantitative form in the Stoner stability criterion against magnetism [17,18]. In the SCRO case, one might imagine a significantly more narrow Re $5d$ band than in pure Re metal due to the different chemical environment. A narrow Re $5d$ band, in turn, could then give rise to a higher Re $5d$ density of states at the Fermi level which could provoke spin polarization. In order to test this idea, we calculated the nonmagnetic density of states for SCRO and pure Re metal in the hcp structure [19]. The relevant DOS are plotted in fig. 3, where it can be seen that the SCRO Re $5d$ DOS is actually *lower* than the hcp Re $5d$ DOS at the Fermi level. Assuming that the Stoner exchange integral is roughly the same for Re in the two systems, this implies that the Re moment in SCRO is induced and not intrinsic.

In conclusion, we have presented XAS and XMCD spectra calculated from first principles for SCRO, and calculated the spin and orbital moments both self-consistently and through the use of the XMCD sum rules. Our results suggest that the XMCD sum rules work well for Re. We base this conclusion on the fact that the self-consistent and sum-rule–calculated m_l/m_s ratios are almost identical. In contrast, at the Cr site, the sum rules appear to work less well. We suggest that this is due to cancellation: the orbital moment is calculated by taking the difference between two rather large numbers (the areas of the XMCD peaks at the L_2 and L_3 edges) to get a much smaller number (the orbital moment). For Cr, the orbital moment is very small, and consequently the uncertainty in the resulting number becomes large. Furthermore, our analysis of the nonmagnetic DOS suggests that the Re moment is induced and not intrinsic in SCRO.

Most recently, De Teresa and coworkers have measured saturation magnetic moments for SCRO using high fields of 20–30 T, corrected for anti-site disorder [20]. They found a saturation magnetic moment of $1.38\,\mu_B$ per unit cell in a (hypothetical) highly ordered SCRO crystal. This is significantly larger than earlier measurements ($0.95\,\mu_B$) and compares well with our theoretical results for the perfectly ordered system. The remaining discrepancies between the theoretical and experimental results presented here can be due to many things, *e.g.*, anti-site disorder, nonsaturated magnetism, temperature effects, or to the insufficient description of strong correlation effects.

* * *

GV, VK and AD acknowledge financial support from VR, KAW/KVA and SSF grants, and MA from the ANR-06-NANO-053-01 grant. SNIC and CINES (project gem1100) are acknowledged for providing supercomputer time.

REFERENCES

[1] Serrate D., De Teresa J. M. and Ibarra M. R., *J. Phys.: Condens. Matter*, **19** (2007) 023201; Bibes M. and Barthélémy A., *IEEE Trans. Electron. Dev.*, **54** (2007) 1003.

[2] Kobayashi K. I., Kimura T., Sawada H., Terakura K. and Tokura Y., *Nature (London)*, **395** (1998) 677.

[3] Chioncel L., Arrigoni E., Katsnelson M. I. and Lichtenstein A. I., *Phys. Rev. Lett.*, **9** (2006) 137203.

[4] Krockenberger Y., Mogare K., Reehuis M., Tovar M., Jansen M., Vaitheeswaran G., Kanchana V., Bultmark F., Delin A., Wilhelm F., Rogalev A., Winkler A. and Alff L., *Phys. Rev. B*, **75** (2007) 020404(R); Majewski P., Geprägs S., Boger A., Opel M., Erb A., Gross R., Vaitheeswaran G., Kanchana V., Delin A., Wilhelm F., Rogalev A. and Alff L., *Phys. Rev. B*, **72** (2005) 132402.

[5] Kato H., Okuda T., Okimoto Y., Tomioka Y., Takenoya Y., Ohkubo A., Kawasaki M. and Tokura Y., *Appl. Phys. Lett.*, **81** (2002) 328; Kato H., Okuda T., Okimoto Y., Tomioka Y., Oikawa K., Kamiyama T. and Tokura Y., *Phys. Rev. B*, **65** (2002) 144404.

[6] Vaitheeswaran G., Kanchana V. and Delin A., *Appl. Phys. Lett.*, **86** (2005) 032513; *J. Phys. Conf. Ser.*, **29** (2006) 50.

[7] Thole B. T., Carra P., Sette F. and van der Laan G., *Phys. Rev. Lett.*, **68** (1992) 1943; Carra P., Thole B. T., Altarelli M. and Wang X., *Phys. Rev. Lett.*, **70** (1993) 694.

[8] Wills J. M., Eriksson O., Alouani M. and Price O. L., in *Electronic Structure and Physical Properties of Solids*, edited by Dreyssé H. (Springer, Berlin) 2000.

[9] Alouani M., Wills J. M. and Wilkins J. W., *Phys. Rev. B*, **57** (1998) 9502; Alouani M. and Wills J. M., in *Electronic Structure and Physical Properties of Solids*, edited by Dreyssé H. (Springer, Berlin) 2000.

[10] Kanchana V., Vaitheeswaran G., Alouani M. and Delin A., *Phys. Rev. B*, **75** (2007) 220404(R).

[11] Kanchana V., Vaitheeswaran G. and Alouani M., *J. Phys.: Condens. Matter*, **18** (2006) 5155.

[12] Oppeneer P. M., *J. Magn. & Magn. Mater.*, **188** (1998) 275; see also Souza I. and Vanderbilt D., *Phys. Rev. B*, **77** (2008) 054438.

[13] Majewski P., Geprägs S., Sanganas O., Opel M., Gross R., Wihelm F., Rogalev A. and Alff L., *Appl. Phys. Lett.*, **87** (2005) 202503.

[14] Galanakis I., Ostanin S., Alouani M., Dreyssé H. and Wills J. M., *Phys. Rev. B*, **61** (2000) 4093.

[15] Soderlind P. *et al.*, *Phys. Rev. B*, **45** (1992) 12911; Soderlind P., *J. Alloys Compd.*, **444** (2007) 93.

[16] Ebert H., private communication.

[17] Stoner E. S., *Proc. R. Soc. London, Ser. A*, **165** (1938) 372.

[18] Grechnev G. E., Panfilov A. S., Svechkarev I. V., Delin A., Johansson B., Wills J. M. and Eriksson O., *J. Magn. & Magn. Mater.*, **192** (1999) 137.

[19] For the nonmagnetic calculations we have used The Stuttgart TB-LMTO-ASA code, version 4.7. See url `http://www.fkf.mpg.de/andersen/`.

[20] De Teresa J. M., Michalik J. M., Blasco J., Algarabel P. A., Ibarra M. R., Kapusta C. and Zeitler U., *Appl. Phys. Lett.*, **90** (2007) 252514.