X-ray magnetic circular dichroism study of Re 5d magnetism in Sr$_2$CrReO$_6$

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We have measured Re 5d spin and orbital magnetic moments in the ferrimagnetic double perovskite Sr$_2$CrReO$_6$ by X-ray magnetic circular dichroism at the $L_2,3$ edges. In fair agreement with recent band-structure calculations, at the Re site a large 5d spin magnetic moment of $-0.68 \mu_B$ and a considerable orbital moment of $+0.25 \mu_B$ have been detected. We found that the Curie temperature of the double perovskites $A_2BB'O_6$ scales with the spin magnetic moment of the 'non-magnetic' B' ion.

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Among the ferrimagnetic double perovskites, which are currently considered as possible spintronics materials, the compound Sr$_2$CrReO$_6$ with its Curie temperature $T_C$ of about 635 K has the highest transition temperature observed so far in this class of materials. The physical mechanism leading to the high Curie temperature is still unclear. Compared to the related double perovskites Sr$_2$CrWO$_6$ and Sr$_2$FeReO$_6$ with $T_C \approx 460$ K and $T_C \approx 400$ K respectively, Sr$_2$CrReO$_6$ has a considerably increased $T_C$. From a recent neutron diffraction study of the mixed compounds Sr$_2$Fe$_{1-x}$Cr$_x$ReO$_6$, it was speculated that the cation size matching improves with increasing $x$. This in turn increases the $pd$ hybridization, contributing to an enhancement of $T_C$. These observations can at least qualitatively be understood within a generalized double exchange or kinetic energy driven exchange model proposed by Sarma et al., where the itinerant electrons mediate an indirect antiferromagnetic coupling between the Cr or Fe and the W or Re moments.

It is still an open question whether the magnetic moments at the 'non-magnetic' W/Re sites are induced by the hybridization with the magnetic 3d ion or intrinsic 5d moments. It has been suggested recently that the critical temperature in this type of ferrimagnetic double perovskites scales with the magnetic moment of the 'non-magnetic' site. An important experimental test for this idea is the investigation of the spin and orbital magnetic moments at the Re site in Sr$_2$CrReO$_6$ with its unexpectedly high transition temperature. Band-structure calculations based on the full-potential linear muffin-tin orbital method predict a value for the Re spin magnetic moment of $-0.85 \mu_B$ or $-0.69 \mu_B$ using the generalized gradient approximation (GGA) or local spin density approximation (LSDA), respectively, both with included spin-orbit (SO) coupling. First experimental results from neutron scattering indicate a much smaller value of about $-0.21 \mu_B$ at 5 K. However, it is of great importance to measure directly magnetic moments with a state-of-the-art method as X-ray magnetic circular dichroism (XMCD). The great advantage of XMCD is its element selectivity and the possibility to extract spin and orbital magnetic moments using the magneto-optical sum-rules. A considerable orbital magnetic moment on Re is also predicted by theory ($0.18 \mu_B$), indicating the relevance of spin-orbit-coupling which leads, in turn, to a break-down of the complete half-metallicity in Sr$_2$CrReO$_6$. In contrast, in Sr$_2$CrWO$_6$ and Sr$_2$FeMoO$_6$ the half-metallic character is preserved.

In this letter, we present a XMCD study of the Re moments in Sr$_2$CrReO$_6$ polycrystalline bulk samples supplemented by SQUID (superconducting quantum interference device) magnetization measurements. Our measurements give further evidence that the Curie temperature $T_C$ in the ferrimagnetic double perovskites of the form $A_2BB'O_6$ with $A$ an alkaline earth, $B$ a magnetic metal, and $B'$ an originally non-magnetic 3d or 5d metal is strongly dependent on the magnetic moment at the $B'$ site.

The samples were made from a stoichiometric mixture of SrO$_2$, Re, and CrO$_2$ powders encapsulated in an evacuated silica tube. The powder was sintered with temperature increased stepwise up to 850°C before pressed to a pellet. This pellet was again sintered in an evacuated silica tube at 1150°C for four days using Ni as getter material. The final samples contain only a tiny amount of elemental Re as seen by x-ray diffraction using a four circle geometry. From Rietveld-analysis we estimate the amount of elemental Re less than 3%. The
amount of Cr/Re antisites is about 9%. From SQUID measurements we obtained $T_C = 635$ K for Sr$_2$CrReO$_6$ and a saturation magnetization $M_{sat} \approx 0.89 \mu_B/\text{f.u.}$.

The XMCD measurements on the Re L$_{2,3}$ edges were performed at the European Synchrotron Radiation Facility (ESRF) at beam line ID12 [16]. The spectra were normalized at 5 K and a saturation magnetization curve in Fig. 1. The XANES spectra recorded with opposite helicities of the incoming X-ray beam. To ensure that the XMCD measurements were obtained for both directions of the applied magnetic field measured at the Re L$_{2,3}$ edges for the double perovskites Sr$_2$FeMoO$_6$ [18] and A$_2$CrWO$_6$ ($A = \text{Ca, Sr}$) [11].

As shown in Fig. 2 for both absorption edges we find a rather intense XMCD signal. This is a clear evidence for the existence of a magnetic moment at the Re 5d shell. We have extracted spin and orbital moments, $m_S$ and $m_L$, of Re and summarized in Table I. Note that in order to obtain the spin and orbital magnetic moments separately the data must be normalized to the number of 5d holes $n_h$. According to band-structure calculations we use $n_h = 5.3$ [19]. This has to be kept in mind when comparing data, as $n_h$ is proportional to the obtained moments. Only the ratio $m_L/m_S$ is independent of the estimate of $n_h$. Both, $m_L/m_S$ and $m_s$, are clearly larger than expected from the calculations including spin-orbit coupling. This underlines the importance of relativistic effects for the heavy Re.

Table I: Summary of magnetic moments at the ‘non-magnetic’ ion Re in Sr$_2$CrReO$_6$ ($T_C = 635$ K) measured by XMCD using $n_h = 5.3$. For comparison calculated values with different approximations to the exchange integral are also shown.

| Method      | $m_S$ (µB/Re) | $m_L$ (µB/Re) | $|m_L/m_S|$ |
|-------------|---------------|---------------|------------|
| experiment  | -0.68         | 0.25          | 0.37       |
| LSDA+SO [11]| -0.69         | 0.17          | 0.25       |
| GGA+SO [11] | -0.85         | 0.18          | 0.21       |

In Fig. 3 we summarize currently published data for the spin moment of $B' = \text{Mo, Re}$ to investigate the relation of Curie temperature $T_C$ and spin magnetic moment $m_S$ at the B$'$ site of the ferrimagnetic double perovskites of the type A$_2$BB'O$_6$. The data suggests that indeed $T_C$ scales with $m_S$ at the B$'$ site. Of course, we cannot draw final conclusions from this comparison as other factors as structure, hybridization, and site occupation can strongly influence the magnetic properties.

We now discuss the XANES spectra of Sr$_2$CrReO$_6$ shown in Fig. 2. The white lines at the Re L$_{2,3}$ edges have a fine structure which reflects the Re 5d density of unoccupied states influenced by the crystal field. The white lines at both edges show a faint shoulder on the high energy side. This can be interpreted as the signature of the crystal field splitting of the 5d band into $t_{2g}$ and $e_g$ states ($\sim 3$ eV). More pronounced double peak structures of similar splitting have been already observed at the Mo L$_{2,3}$ and W L$_{2,3}$ edges for the double perovskites Sr$_2$FeMoO$_6$ [18] and A$_2$CrWO$_6$ ($A = \text{Ca, Sr}$) [11].
Figure 3: (Color online) $B'$ spin magnetic moments for different double perovskites $A_2BB'O_6$ measured by XMCD on Mo [18], our data on W [11] and Re data presented in this paper. The number of $5d$ holes has been obtained from recent bandstructure calculations [1,11,12]. In the inset further data deduced from XMCD [12] using a surprisingly high number of $5d$ holes $n_h > 8$ are shown.

influence $T_C$ [4,20]. However, there is a clear trend that a large $T_C$ is accompanied by a large magnetic moment $m_B$ at the $B'$ site. This finding is in qualitative agreement with the simple model of ferrimagnetism mediated by itinerant minority spin carriers. In the inset of Fig. 7 we show recent XMCD data on other Re-based double perovskites which show the similar trend [12]. The relatively high values of the spin magnetic moment for these samples are mainly due to the rather high number of $d$-holes used in their data analysis. Nevertheless our data and those of [12] follow satisfactorily the scaling law of Curie temperature and spin magnetic moment at the $B'$ site. We emphasize that $T_C$ seems not to depend on the total spin moment given by the sum of the local moment on the magnetic $B$ site (Cr, Fe) and the induced magnetic moment on the non-magnetic $B'$ site (Mo, W, Re). If this would be the case, different $T_C$ values would be expected for the Cr and Fe based double perovskites in contrast to the experimental data.

In summary, we have unambiguously demonstrated a large spin magnetic moment at the Re $5d$ site in the ferrimagnetic double perovskite Sr$_2$CrReO$_6$ together with a considerable orbital magnetic moment. This result together with data from literature suggest that the critical temperature for such double perovskites scales with the magnetic moment at the ‘non-magnetic’ site of the compound. The data is in fair agreement with the model prediction and is important for understanding the mechanism of the high Curie temperatures in the ferrimagnetic double perovskites.

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[1] G. Vaitheeswaran, V. Kanchana, and A. Delin, Appl. Phys. Lett. 86, 032513 (2005).
[2] H. Kato, T. Okuda, Y. Okimoto, Y. Tomioka, Y. Takenoya, A. Okhuku, M. Kawasaki, and Y. Tokura, Appl. Phys. Lett. 81, 328 (2002).
[3] H. Asano, N. Kozuka, A. Tsuzuki, and M. Matsui, Appl. Phys. Lett. 85, 263 (2004).
[4] H. Kato, T. Okuda, Y. Okimoto, Y. Tomioka, K. Oikawa, T. Kamiyama, and Y. Tokura, Phys. Rev. B 69, 184412 (2004).
[5] J. B. Philipp, D. Reisinger, M. Schonecke, A. Marx, A. Erb, L. Alff, R. Gross, and J. Klein, Appl. Phys. Lett. 79, 3654 (2002).
[6] 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, Phys. Rev. B 68, 144431 (2003).
[7] K.-I. Kobayashi, T. Kimura, Y. Tomioka, H. Sawada, K. Terakura, and Y. Tokura, Phys. Rev. B 59, 11159 (1999).
[8] N. Auth, G. Jakob, W. Westerburg, C. Ritter, I. Bonn, C. Felser, and W. Treml, J. Magn. Magn. Mater. 272-276, 607(2004).
[9] J. M. De Teresa, D. Serrate, C. Ritter, J. Blasco, M. R. Ibarra, L. Alff, R. Gross, G. Vaitheeswaran, V. Kanchana, A. Delin, F. Wilhelm, A. Rogalev, and L. Alff, cond-mat/0506048.
[10] M. Sikora, D. Zajac, Cz. Kapusta, M. Borowiec, C. J. Oates, V. Prochazka, D. Rybicki, J. M. De Teresa, C. Marquina, and M. R. Ibarra, cond-mat/0503358.
[11] B.T. Thole, P. Carra, F. Sette, and G. van der Laan, Phys. Rev. Lett. 68, 1943 (1992).
[12] P. Carra, B.T. Thole, M. Altarelli, and X. Wang, Phys. Rev. Lett. 70, 694 (1993).
[13] K.-I. Kobayashi, T. Kimura, H. Sawada, K. Terakura, and Y. Tokura, Nature 395, 677 (1998).
[14] A. Rogalev, J. Goulon, Ch. Goulon-Ginet, and C. Malgrange, in Magnetism and Synchrotron Radiation, E. Beaurepaire et al. (Eds.), LNP vol. 565 (Springer, 2001).
[15] B. L. Henke, E. M. Gullikson, and J. C. Davis, At. Data Nucl. Data Tables 54, 181-342 (1993). Online available: http://www-cxro.lbl.gov. Using the Chantler tables (online available: http://physics.nist.gov/ffast) the results change by not more than ±4%.
[16] M. Besse, V. Cros, A. Barthélémé, H. Jaffrès, J. Vogel, F. Petroff, A. Mirone, A. Tagliaferri, P. Bencok, P. Decorse, P. Berthet, Z. Szotek, W.M. Temmerman, S.S. Dhesi, N.B. Brookes, A. Rogalev, and A. Fert, Europhys. Lett. 60, 608 (2002).
[17] A. Delin, G. Vaitheeswaran, V. Kanchana, private communication.
[18] J. M. De Teresa, D. Serrate, J. Blasco, M. R. Ibarra, and L. Alff, Phys. Rev. B 69, 144401 (2004).