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Magnetism in Re-based ferrimagnetic double perovskites

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Abstract. We have investigated spin and orbital magnetic moments of the Re 5d ion in the double perovskites $A_2\text{FeReO}_6$ ($A = \text{Ba}, \text{Sr}, \text{Ca}$) by x-ray magnetic circular dichroism (XMCD) at the Re $L_{2,3}$ edges. In these ferrimagnetic compounds, an unusually large negative spin and positive orbital magnetic moment at the Re atoms was detected. The presence of a finite spin magnetic moment in a ‘non-magnetic’ double perovskite as observed in the double perovskite $\text{Sr}_2\text{ScReO}_6$ proves that Re has also a small, but finite *intrinsic* magnetic moment. We further show for the examples of Ba and Ca that the usually neglected alkaline earth ions undoubtedly also contribute to the magnetism in the ferrimagnetic double perovskites.

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1. Introduction

Ordered double perovskites of the composition A_2MNO_6 (with A an alkaline earth, M a magnetic transition metal ion and N a non-magnetic ion) have come again into the focus of research because of their interesting magnetic properties. Firstly, in Sr_2FeMoO_6 a large room-temperature magnetoresistance was observed [1]. Secondly, within the group of ferrimagnetic double perovskites materials with higher Curie temperatures, T_C , than in the simple perovskites (e.g. doped manganites) can be obtained. At the moment, the highest T_C values have been reported for Sr_2CrReO_6 ($T_C \approx 635$ K) [2]–[4] and Sr_2CrOsO_6 ($T_C \approx 725$ K) [5]–[7]. Thirdly, the mechanism leading to magnetic coupling is believed to be associated with a strong tendency to a half-metallic nature of the charge carriers at the Fermi level [8]–[10]. Clearly, these materials are interesting candidates for spintronic applications [11], in particular, when having in mind fully epitaxial structures based on perovskite materials.

Recently, Majewski *et al* and Sikora *et al* have proposed a simple scaling law between the Curie temperature and the induced magnetic moment at the non-magnetic site in the double perovskite structure [4, 12, 13]. Philipp *et al* have discussed that a high Curie temperature is associated with a tolerance factor close to one for the corresponding crystal [14]. The only exception for this rule is found in the series A_2FeReO_6 ($A = Ba, Sr, Ca$). In this particular FeRe-system, it is the strongly monoclinically distorted Ca-based compound having an anomalously high T_C , namely about 540 K [15]–[17] (compared to about 400 K for Sr_2FeReO_6 [16] and 325 K for Ba_2FeReO_6 [18, 19]). The dimensionless tolerance factor, f , in A_2FeReO_6 whose deviation from unity implies structural distortion varies from about $f = 1.057$ for $A = Ba$ over $f = 0.997$ for $A = Sr$ to $f = 0.943$ for $A = Ca$ [14]. In general, the Ba-based ferrimagnetic double perovskites are close to a structural transition into a hexagonal lattice where ferro(i)magnetism is not allowed for symmetry reasons; the Sr-based compounds are always close to a perfect cubic structure with maximal T_C , and the Ca-based double perovskites are orthorhombically or monoclinically distorted, with still a large but—due to the reduced exchange—clearly reduced ferrimagnetic transition temperature. The exceptional large T_C of Ca_2FeReO_6 is accompanied by an insulating state at low temperatures, in contrast to Sr_2FeReO_6 or even the similarly monoclinically distorted Ca_2FeMoO_6 , which both are metallic [20]. The metal–insulator transition in Ca_2FeReO_6 has been reported to occur between 100 and 150 K [15, 16, 20]. This behavior has been attributed to strongly enhanced electron–electron correlations on the Re site due to a reduced transfer integral between Fe and Re corresponding to an extremely large effective Coulomb repulsion, U_{eff} , of about 4 eV on both ions [20]. This, however, is in some contradiction to the observed high Curie temperature, which is believed to

Table 1. Summary of sample properties from x-ray diffraction at 300 K (calculated by Rietfeld refinement) and SQUID magnetometry.

Material	T_C (K)	Symm.	Lattice (\AA)	Antisites (%)
Ba ₂ FeReO ₆	317	Fm $\bar{3}$ m	$a = 8.0571(2)$	0.9
Sr ₂ FeReO ₆	418	Fm $\bar{3}$ m	$a = 7.8752(4)$	2.6
Ca ₂ FeReO ₆	556	P2 ₁ /n	$a = 5.3992(2)$ $b = 5.5269(2)$ $c = 7.6826(3)$	3.6
Sr ₂ ScReO ₆	–	P2 ₁ /n	$a = 5.6760(2)$ $b = 5.6534(2)$ $c = 7.9862(3)$	7

be a consequence of a kinetic energy gain due to the hybridization of the Fe 3d and Re 5d t_{2g} -orbitals. The prediction that a decreased band-filling is favorable for T_C [21], which could be used to reconcile a high T_C with a reduced Re–Re overlap, has turned out to be invalid: an increased band-filling actually leads to a strong T_C enhancement for both the FeMo system [22] and the CrW system [23, 24]. Within the kinetically driven exchange model [8]–[10], the increase of T_C is more naturally explained as a consequence of increased band-filling. Note that the cases of Ca₂FeReO₆ and Sr₂CrOsO₆, both being insulating and having a high T_C at the same time, are completely different. In the case of Sr₂CrOsO₆ having only a tiny rhombohedral distortion, the Os 5d t_{2g} band is completely filled, while for Ca₂FeReO₆ it is the structural distortion that drives the metal–insulator transition. Recently, it was suggested that in double perovskites with heavy ions such as Re a large orbital contribution to the magnetic moment leads to an enhanced total magnetization above the integer value that is expected for a half-metallic material [25]. This elsewhere predicted and calculated [26] strong influence of spin–orbit coupling leads to a quasi-half metallicity, which still is from the viewpoint of applications in spintronics very high (above 90%). Another point of interest is the possibility of an *intrinsic* enhancement of the Re spin magnetic moment due to the peculiar Re⁵⁺ state in the ferrimagnetic double perovskites. In this study, we present the XMCD analysis of the system A₂FeReO₆ (A = Ba, Sr, Ca), compare the experimental data to theoretical predictions calculated within the full-potential linear muffin–tin orbital method (FP-LMTO) [27] with included spin–orbit coupling, and complete the so far suggested scaling law [4] by using the identical method to extract separately spin and orbital magnetic moments. Furthermore, we search for a contribution of the alkaline earth element to the magnetic behavior, and also look for an *intrinsic* Re moment in a suitable double perovskite compound with M being a non-magnetic ion: Sr₂ScReO₆.

2. Experimental

A summary of the sample properties is given in table 1. All values where a comparison can be made to literature values are in good agreement with these data [2, 15]. Note that the small amount of antisite disorder does not affect our results. The XMCD measurements on the Re $L_{2,3}$ edges were performed at the European Synchrotron Radiation Facility (ESRF) at beam line ID12 [29]. The spectra were recorded within the total fluorescence yield detection mode. The XMCD spectra were obtained as direct difference between consecutive XANES scans

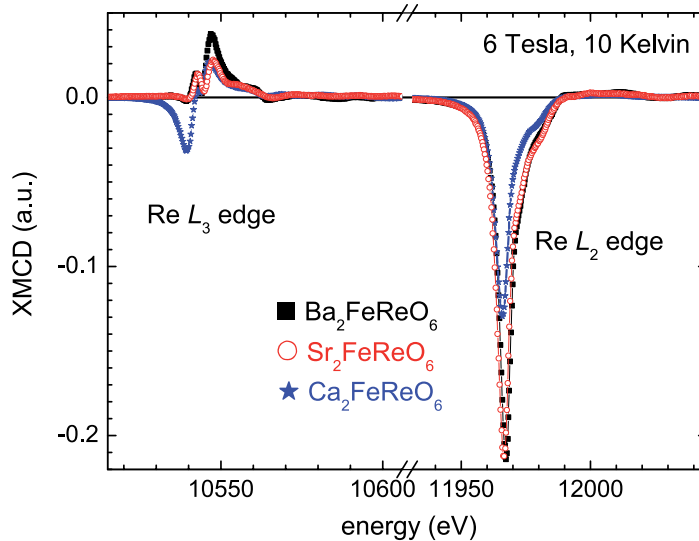


Figure 1. XMCD spectra for $A_2\text{FeReO}_6$ ($A = \text{Ba}, \text{Sr}, \text{Ca}$).

(x-ray absorption near edge spectrum) recorded with opposite helicities of the incoming x-ray beam. To ensure that the XMCD spectra are free from any experimental artifacts, the data were collected for both directions of the applied magnetic field of 6 T (parallel and antiparallel to the x-ray beam). The degree of circular polarization of the monochromatic x-ray beam was 98%. The measurements were performed at about 10 K for all samples ($T \ll T_C$), if not indicated otherwise. Since the samples measured in backscattering geometry were very thick, the spectra were first normalized to the edge jump of unity and then corrected for self-absorption effects. The edge jump intensity ratio L_3/L_2 was then normalized to 2.19/1 [30]. This is different from the statistical 2:1 branching ratio due to the difference in the radial matrix elements of the $2p_{1/2}$ to $5d(L_2)$ and $2p_{3/2}$ to $5d(L_3)$ transitions. The XMCD measurement as a function of applied field suggests that our samples are closer to saturation at 6 T as is concluded by de Teresa *et al* [25] from high-field SQUID measurements. This issue has to be clarified in future by high-field XMCD measurements.

3. Results and discussion

In this paper, the XANES spectra themselves are not further discussed. As shown in figure 1, for FeRe-compounds at both absorption edges we find a rather intense XMCD signal. This is clear evidence for the existence of a magnetic moment at the Re 5d shell. For all three compounds, the XMCD spectra at the L_2 edge are largest (as expected for $m = 1$ orbitals) and similar in shape. In $\text{Ca}_2\text{FeReO}_6$, the size of the XMCD signal is by a factor of 2 smaller compared to the two other FeRe compounds. At the L_3 edge, the Ca-based double perovskite again stands out by a pronounced peak with negative XMCD signal, which is absent for $\text{Sr}_2\text{FeReO}_6$ and $\text{Ba}_2\text{FeReO}_6$. The data at the L_3 edge look slightly different in amplitude as compared to previously published data [13]. However, the data are consistent, in that the integrated XMCD intensity at the L_3 edge is negative only in the case of $\text{Ca}_2\text{FeReO}_6$. In this sense, all data support the unusual behavior of $\text{Ca}_2\text{FeReO}_6$, which cannot only be attributed to the different ionic size of the A site ions.

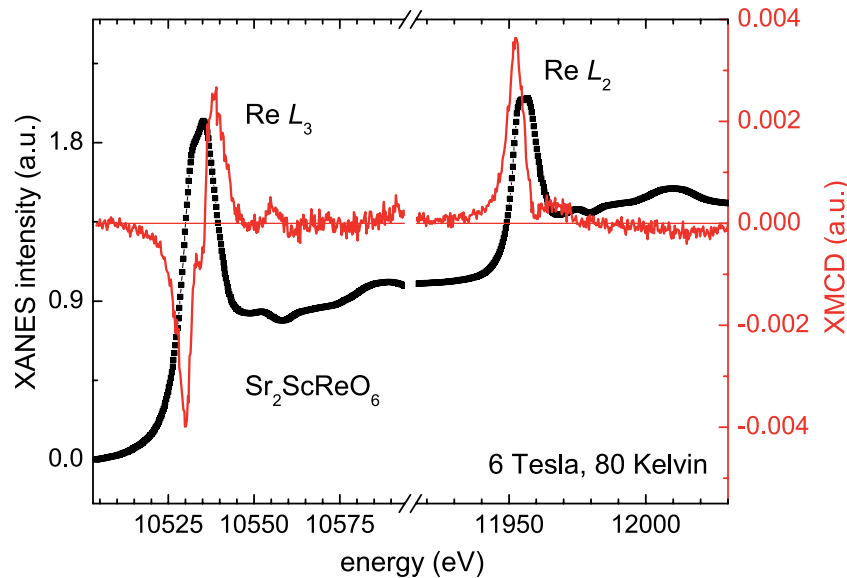


Figure 2. XANES and derived XMCD spectra at the Re L_2 and L_3 edges of $\text{Sr}_2\text{ScReO}_6$.

In figure 2, we show XANES and XMCD spectra for the compound $\text{Sr}_2\text{ScReO}_6$. This compound is important because the absence of any free electrons at Sc^{3+} which has a $3d^0$ configuration will lead to a complete breakdown of the *induced* magnetic moment at the Re site. This compound therefore allows the measurement of the *intrinsic* magnetic moment of Re^{5+} (also in contrast to Re^{6+} compounds such as $\text{Sr}_2\text{MgReO}_6$). Previously, Kato *et al* have calculated from a Curie–Weiss fit to the susceptibility an effective magnetic moment of Re in $\text{Sr}_2\text{ScReO}_6$ of about $1.1 \mu_B/\text{f.u.}$, as expected within the ionic picture [32]. In contrast, our data show the existence of a much smaller, but finite intrinsic moment at the Re site, indicating an increased tendency to magnetic ordering of Re^{5+} . Since this moment is present above the antiferromagnetic transition temperature, it is not related to spin glass behavior. The spin magnetic moment is about 50 times smaller than corresponding induced moments on Re^{5+} , and the orbital magnetic moments even by a factor of 100. However, due to the high sensitivity of the set-up at ESRF, one can unambiguously prove the existence of this moment. In contrast to the opposite sign of the induced magnetic moment with respect to the applied field, the spin magnetic moment at the Re in $\text{Sr}_2\text{ScReO}_6$ is aligned with the field. This is expected because the kinetic exchange via fully polarized spin down electrons is not at work. This intrinsic moment of Re^{5+} therefore has to be considered as an indicator of the tendency to unusually high magnetization of Re-based double perovskites.

As a last point, we address magnetism in the earth alkaline ions themselves, which usually are completely neglected in the magnetic scenario. The XANES and XMCD spectra of the Ba L_2 and L_3 edges of $\text{Ba}_2\text{FeReO}_6$ and of the Ca K -edge of $\text{Ca}_2\text{FeReO}_6$ are shown in figure 3. The 5d spin magnetic moment (calculated with 9 as the number of d-holes corresponding to the band-structure calculation) of Ba is $\mu_S = -0.0065$ and the 5d orbital magnetic moment $\mu_L = -0.0013$ (both in $\mu_B/\text{f.u.}$), $|\mu_L/\mu_S| \approx 0.2$. The theoretical predictions calculated as described elsewhere [26, 28] are $\mu_S = -0.0084$ and $\mu_L = -0.0014$, which is in fair agreement with our experimental data. For $\text{Ca}_2\text{FeReO}_6$, we can only qualitatively say that a finite magnetic

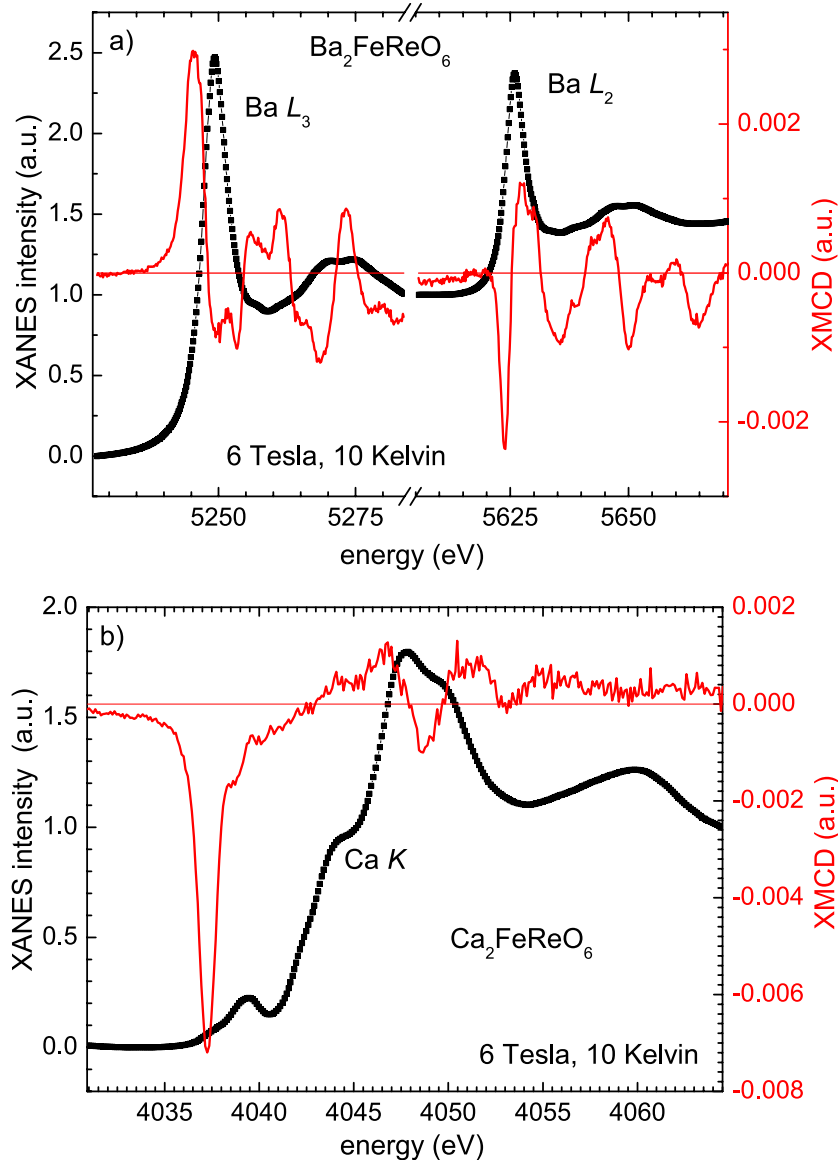


Figure 3. XANES and derived XMCD spectra (a) at the Ba L_2 and L_3 edges of $\text{Ba}_2\text{FeReO}_6$ and (b) at the Ca K edge of $\text{Ca}_2\text{FeReO}_6$.

moment is observed, because the K -edge probes only the 4p orbital magnetism. Since the L edges are experimentally not accessible, a quantitative analysis cannot be done. The observation of a magnetically polarized density of states gives clear evidence for a magnetic interaction of the earth alkaline ions with the other ions. The magnetic contribution of Ba in this case is a factor of 2 smaller than the contribution of the intrinsic Re moment. Naturally, one expects that the magnetic contribution increases with ionic size due to the increased exchange with the neighboring ions. The clear orbital contribution in $\text{Ba}_2\text{FeReO}_6$ is not unexpected due to the heavy ionic mass. Our data provide a test for a detailed theoretical study of the magnetism in the double perovskites, and underline the importance of taking spin-orbit coupling into account. Note that for example in CrO_2 where the importance of oxygen in the magnetic mechanism

Table 2. Measured (exp., normalized to 5 K) and calculated (th., calculated within the generalized gradient approximation including spin–orbit coupling (GGA+SO)) magnetic moments at the Re site for different double perovskites at about 10 K. For a detailed discussion of the applied band-structure calculation, see e.g. [26, 28]. Calculation in [31] is GGA *with* spin–orbit coupling. The number of d-holes was taken from the band-structure calculation. In our case this number was around 5.3. The error of the measured values is estimated as 2.5%.

	Material	m_S ($\mu_B/f.u.$)	m_L ($\mu_B/f.u.$)	$ m_L/m_S $
exp.	Ba ₂ FeReO ₆	−0.56	0.15	0.27
	Sr ₂ FeReO ₆	−0.74	0.21	0.28
	Ca ₂ FeReO ₆	−0.47	0.16	0.34
	Sr ₂ CrReO ₆ [4]	−0.68	0.25	0.37
	Sr ₂ ScReO ₆ (80 K)	0.013	−0.002	0.15
th.	Ba ₂ FeReO ₆	−0.65	0.19	0.29
	Sr ₂ FeReO ₆	−0.68	0.15	0.22
	Sr ₂ FeReO ₆ [31]	−0.85	0.23	0.27
	Sr ₂ CrReO ₆ [26]	−0.85	0.18	0.21

is undoubted, comparable values of spin and orbital moments of the oxygen ion have been measured [33] as compared to our results on Ba in Ba₂FeReO₆.

In table 2, we summarize our results for the spin and orbital magnetic moments at the Re site as derived from the XMCD measurements by applying the standard sum rules [34, 35] and compare them with theoretical values. Also, the ratio $|m_L/m_S|$ is calculated, since this quantity is not affected by possible uncertainties in the calculated number of holes. In general, the calculated data are in surprisingly good agreement with the measured data. One of the main reasons certainly is that spin–orbit coupling is taken into account from the beginning. Note that in the hard x-ray range the sum rules apply with high validity due to the large spin–orbit splitting of the core level.

Let us finally discuss again our data for the three FeRe-based compounds. Our data are in good qualitative and quantitative agreement with literature data with one exception: Ca₂FeReO₆. While Sikora *et al* [13] find that the spin magnetic moment of Re in Ca₂FeReO₆ scales with the high T_C , in our case it has the lowest spin magnetic moment, letting Ca₂FeReO₆ stand out from the scaling law [4, 12, 13] which so far holds in all other cases. This behavior is certainly more natural, since one expects that a reduced exchange will also lead to a reduced spin magnetic moment on the Re site. Note that the ratios of orbital and spin magnetic moments are consistent with the previous data. As suggested previously by Kato *et al* [16], a Re t_{2g} orbital ordered state or its glass-state analogue associated with the monoclinic lattice distortion occurs, pointing out the importance of correlation effects in this compound. Recently, Sikora *et al* [36] proposed a scenario with a complex competition between two phases with different electronic and crystallographic structure. Our data give further indication that Ca₂FeReO₆ is exceptional among the double perovskites due to the strong octahedral-site distortions.

4. Summary

In summary, we have elucidated the Re magnetic moments in the FeRe-based series of double perovskites as a function of the earth alkaline ion, confirming the exceptional position of $\text{Ca}_2\text{FeReO}_6$. We have measured a finite *intrinsic* magnetic moment at the Re^{5+} site in $\text{Sr}_2\text{ScReO}_6$ indicating the tendency for enhanced magnetic moments observed in Re-based double perovskites. Furthermore, for the first time we were able to measure by XMCD the magnetic moments directly at the alkaline earth site itself. Our result shows that the usually neglected Ca and Ba ions play a role in the magnetic scenario of the kinetically driven exchange model, comparable in size to the role of oxygen.

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