Evidence of unquenched Re orbital magnetic moment in AA'FeReO$_6$ double perovskites

M. Sikora[a]

Department of Solid State Physics, Faculty of Physics and Applied Computer Sciences,
AGH University of Science and Technology, 30-059 Cracow, Poland and European Synchrotron Radiation
Facility, BP 220, 38043 Grenoble Cedex, France

Cz. Kapusta, M. Borowiec, C. J Oates, V. Prochazka, D. Rybicki, and D. Zajac

Department of Solid State Physics, Faculty of Physics and Applied Computer Sciences,
AGH University of Science and Technology, 30-059 Cracow, Poland

J. M De Teresa, C. Marquina, and M. R Ibarra[b]

Departamento de Fisica de la Materia Condensada and Instituto de Ciencia de Materiales de Aragon,
Universidad de Zaragoza—CSIC, 50009 Zaragoza, Spain

Spin and orbital magnetic moments of rhenium in AA'FeReO$_6$ double perovskites (A,A'=Ba, Sr, and Ca) have been directly probed employing x-ray magnetic circular dichroism at the Re $L_{2,3}$ edges. A considerable orbital magnetic moment is observed in all the compounds studied, which confirm theoretical predictions of unquenched Re orbital moment despite its octahedral coordination. Relative orbital-to-spin moment ratio alters with lattice distortion from m_L/m_S= −0.285 to −0.337 from Ba$_2$FeReO$_6$ to Ca$_2$FeReO$_6$, respectively. Moreover, the spin moment of Re ion scales with Curie temperature, the most relevant property in spin electronics application of the compounds studied. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2234292]

Ordered double perovskites have recently attracted great interest due to their large spin polarization and Curie temperature (T_C) much higher than room temperature. These properties are strongly desired in order to realize reasonable magnetoresistance effects at room temperature, which is not only a challenging subject of fundamental science but also an important phenomenon for potential applications in spin electronics. Therefore the first observation of substantial magnetoresistance at room temperature in Sr$_2$FeMoO$_6$ (Ref. 1) quickly led to production of magnetic tunnel junctions and magnetoresistive potentiometers.

Currently, the other ordered double perovskites $AA'BB'$O$_6$ (A,A'=Ca, Sr, Ba, La, etc.; BB'=FeMo, FeRe, CrRe, CrW, etc.) are being intensively studied in order to find a material with optimal performance.[2–7] Among them the Re-based double perovskites are the most promising compounds in terms of high Curie temperature, e.g., 538 and 635 K in Ca$_2$FeReO$_6$ and Sr$_2$CrReO$_6$, respectively.[3] Moreover, Re-based double perovskites are magnetically hard[4,6,8] and reveal large magnetoelastic effects,[9] which can only be explained by a substantial magnetocrystalline anisotropy due to the anisotropy of an unquenched orbital moment of Re.[6]

The aim of the present study was to find out whether a significant Re orbital moment exists in Re–Fe double perovskites and how the lattice distortion influences its value. Moreover, our experiments provide the direct quantitative information about the total magnetic moment of Re ions unlike previous measurements with neutron diffraction,[5] Mössbauer,[2,4] and nuclear magnetic resonance (NMR) spectroscopies,[11] as well as band structure calculations.[10,12,13] For example, the calculated and measured total magnetic

moment of Re is always antiparallel to that of Fe, but its value reported for Sr$_2$FeReO$_6$ ranges from 0.16μ_B to 1.27μ_B. All these issues are addressed by means of the sum rule analysis of the x-ray magnetic circular dichroism (XMCD) spectra, which enables an independent derivation of the spin and orbital contributions to the magnetic moment.[14]

Experiments were carried out on a series of five AA'FeReO$_6$ double perovskites (AA'=Ba$_2$, BaSr, Sr$_2$, SrCa, and Ca$_2$). A detailed description of the preparation route and physical properties of the compounds studied are described in Ref. 6. Rhenium $L_{2,3}$-edge XMCD spectra were measured at the beamline A1 in Hasylab/DESY, Hamburg. All the spectra were recorded at 10 K on polycrystalline samples using a transmission mode in an applied magnetic field up to 20 kOe, flipped at each energy point.

Rhenium $L_{2,3}$ near edge absorption spectra of all the compounds studied have a similar shape to those of Ba$_2$FeReO$_6$, presented in Fig. 1. The measured edge step ratio L_3/L_2 of 2.17(3) is in agreement with the theoretical value.[15] The only difference observed is a gradual edge shift revealed by the decrease of the first moment by 0.4 eV from ReO$_3$ to Ba$_2$FeReO$_6$ and further by 0.15 and 0.3 eV to Sr$_2$FeReO$_6$ and Ca$_2$FeReO$_6$, respectively. This indicates that all the compounds studied reveal an effective valence state lower than Re^{6+}, which decreases with increasing lattice distortion. This is consistent with the Fe valence evolution observed by the Mössbauer spectroscopy.[2,4]

Recently, Jeng and Guo, in their theoretical study of magnetic moments in Sr$_2$FeReO$_6$,[10] found that Re 5d orbital downspin states are highly polarized. Using the orbital occupation numbers, reported in Ref. 10 one can estimate the relative intensity of the XMCD spectra applying oscillator strengths for electronic excitation.[16] According to such an analysis the integrated Re L_3-edge XMCD spectra ought to be positive and ten times less intense than the negative

[a]Electronic mail: sikora@esrf.fr
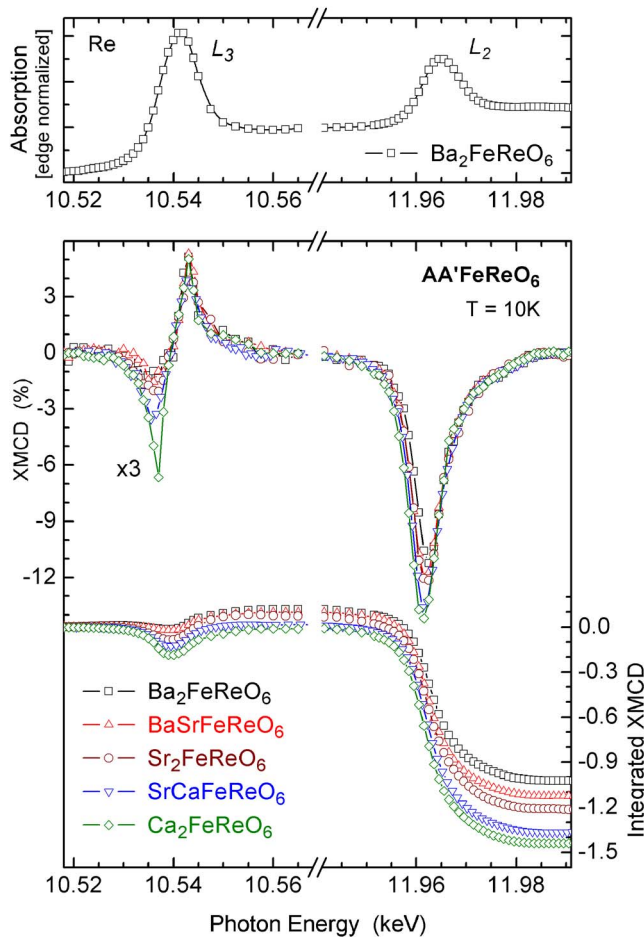[b]Also at: Instituto de Nanociencia de Aragon, Universidad de Zaragoza, Zaragoza, 50009, Spain.

FIG. 1. (Color online) X-ray absorption spectra of Ba_2FeReO_6 (upper panel) together with normalized and integrated (lower panel) Re $L_{2,3}$-edge XMCD spectra of the compounds studied.

L_2-edge spectra. Moreover, if Re $5d$ t_{2g} and e_g subbands are considerably split in energy, the L_3-edge XMCD ought to show a differential-like shape due to negative (positive) contribution from excitation to the t_{2g} (e_g) orbital, whereas the L_2 edge ought to reveal a single broad peak due to negative contribution from both kinds of excitation.

The latter predictions are unambiguously confirmed by our experimental results, presented in Fig. 1. The Re L_3-edge XMCD spectra show a differential-like shape with a minimum at the edge energy and a positive peak close to the white line (WL) maximum. The integrated XMCD at the Re L_3 edge is positive for all the compounds studied except for Ca_2FeReO_6, whereas all the Re L_2-edge XMCD spectra consist of a single broad negative peak. Its amplitude is much larger than the maximum of the L_3-edge signal, as expected for a system with predominantly occupied $m=1$ orbitals. This finding confirms the scenario of an unquenched orbital moment of the Re $5d$ electrons. The main difference in the shape of the spectra between compounds studied is due to a different contribution from the $5d$ t_{2g} subband. This is revealed by the enhancement of the negative peak at the low energy part of L_3 and L_2 edges and a shift of the latter towards lower energy with increasing lattice distortion. The effect corresponds to a change of the t_{2g} band polarization due to the increase of electronic occupation of the spin-down t_{2g} subband.

Orbital, m_L, and spin, m_S, magnetic moments of rhenium were derived from XMCD spectra using the sum rule method.[14] It revealed that the relative orbital-to-spin contribution increases with lattice distortion as presented in Table I and Fig. 2. Note that the m_L/m_S ratio is an independent quantity derived directly from integrals of XMCD spectra, whereas in order to determine absolute values of spin and orbital magnetic moments the white line intensity must be extracted and divided by the number of $5d$ holes, n_h. In the present study the Lorentzian-like WL intensities were derived by subtracting an arctan step function from the absorption spectra. The n_h parameters were obtained from a combined analysis of the WL intensity of the compounds studied and the gold reference foil, similar to that described in Ref. 17. The results correlate well with the observed shifts of the first moment of absorption spectra. Note that the obtained values of n_h, shown in Table I, are close to those expected by an ionic model assuming an iron valence state derived from Mössbauer spectra,[2,4] whereas they are significantly higher than those reported by band structure calculations[10,12] as well as those used in recent XMCD studies of Sr_2CrReO_6.[18] The determined spin and orbital moments of Re are antiparallel,

TABLE I. Orbital (m_L), spin (m_S), and total (m_{tot}) magnetic moments of Re at $T=10$ K in the $AA'FeReO_6$ series. Values are given in μ_B/Re for the number of $5d$ holes (n_h) derived from the x-ray absorption spectra (first line for each compound) and reported in theoretical calculations. The last four columns present the Re spin moment values reported in literature for the compounds studied references in text). They were determined using neutron diffraction (ND) and nuclear magnetic resonance (NMR) as well as calculated using local spin density approximation (LSDA) and generalized gradient approximation (GGA).

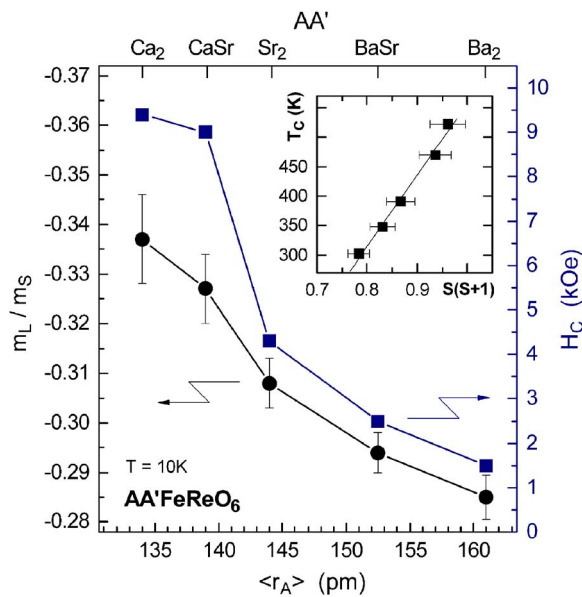| AA'	m_L/m_S	n_h	m_L	m_S	m_{tot}	ND	NMR	LSDA	GGA
Ba_2	−0.285(5)	8.2	0.28(2)	−0.99(6)	−0.71		−0.87	−0.99	
		5.5	0.19(2)	−0.66(5)	−0.47			−1.22	
$BaSr$	−0.294(4)	8.2	0.30(2)	−1.03(7)	−0.73				
Sr_2	−0.308(5)	8.1	0.33(2)	−1.07(7)	−0.74	−0.16(7)	−0.94	−1.05	
		5.6	0.23(2)	−0.74(6)	−0.51			−1.27	
		6.8	0.28(2)	−0.90(7)	−0.62			−0.74	−0.85
								−0.85	−0.96
$SrCa$	−0.327(7)	8.0	0.37(3)	−1.13(8)	−0.76				
Ca_2	−0.337(9)	7.8	0.39(3)	−1.15(9)	−0.76	−0.81(6)	−0.95	−1.07	
		5.8	0.29(2)	−0.86(7)	−0.57	−1.02(7)		−1.33	
						−0.91		−1.12	

FIG. 2. (Color online) The ratio of orbital-to-spin magnetic moment of Re compared with the coercive field of the AA'FeReO$_6$ compounds plotted vs the average radius of alkali earth ions. Inset shows the dependence of Curie temperature vs the effective spin moment of Re ions. Lines are guides for the eyes.

as expected from Hund's third rule. The resulting total Re moment is antiferromagnetically coupled to the Fe moment and amounts to $m_{tot} \approx 0.75 \mu_B$ in good agreement with the recent NMR (Ref. 11) and neutron diffraction results.[5] Surprisingly, the obtained spin moment is of the order of $1.1 \mu_B$ which is accidentally similar to the predictions of band structure calculations.[12,13]

The total magnetic moment of Re in the AA'FeReO$_6$ series is not significantly modified within the series, similar to the bulk magnetization,[6] whereas the orbital moment shows a clear correlation with the lattice distortion (Fig. 2). Moreover, both the spin and the orbital contributions are increasing with lattice distortion, which indicates a strengthening of magnetic interactions. A comparison of the local magnetic moment evolution with the macroscopic magnetic properties of the compounds reveals a correlation with Curie temperature. An approximately linear dependence of T_C on the effective spin moment $S(S+1)$ of Re (see inset of Fig. 2) is similar to that predicted for Heisenberg-like exchange interactions.

In Fig. 2, the behavior of the coercive field and the m_L/m_S ratio is compared. Although the values of both quantities increase with lattice distortion, the relative increase of the orbital contribution is smaller compared with that of the coercive field, which could be attributed to a possible anisotropy of an unquenched iron orbital moment. Thus, an XMCD study of iron orbital moment in these compounds would be advisable in order to confirm this hypothesis.

In summary, the presented study confirms theoretical predictions claiming that Re moment is not quenched by octahedral ligand field in AA'FeReO$_6$ double perovskites. The derived magnetic moment of Re is of the order of $0.75 \mu_B$ and is antiparallel to that of Fe, which agrees well with bulk magnetization and NMR results. The effective total

angular momentum of rhenium does not change significantly within the series, whereas the magnitude of the orbital contribution increases with the lowering of local symmetry of the compounds. Finally, the effective spin moment of Re scales linearly with Curie temperature, which suggests its high importance in the mechanisms leading to high magnetic ordering temperatures in ferrimagnetic double perovskites.

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

[2] J. Gopalakrishnan, A. Chattopadhyay, S. B. Ogale, T. Venkatesan, R. L. Greene, A. J. Millis, K. Ramesha, B. Hannoyer, and G. Marest, Phys. Rev. B **62**, 9538 (2000); S. Nakamura, M. Tanaka, H. Kato, and Y. Tokura, J. Phys. Soc. Jpn. **72**, 424 (2003).

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

[4] T. Alamelu, U. V. Varadaraju, M. Venkatesan, A. P. Douvalis, and J. M. D. Coey, J. Appl. Phys. **91**, 8909 (2002).

[5] W. Westerburg, O. Lang, C. Ritter, C. Felser, W. Tremel, and G. Jakob, Solid State Commun. **122**, 201 (2002); E. Granado, Q. Huang, J. W. Lynn, J. Gopalakrishnan, R. L. Greene, and K. Ramesha, Phys. Rev. B **66**, 064409 (2002); K. Oikawa, T. Kamiyama, H. Kato, and Y. Tokura, J. Phys. Soc. Jpn. **72**, 1411 (2003); J. M. De Teresa, D. Serrate, C. Ritter, J. Blasco, M. R. Ibarra, L. Morellon, and W. Tokarz, Phys. Rev. B **71**, 092408 (2005).

[6] J. M. De Teresa, D. Serrate, J. Blasco, M. R. Ibarra, and L. Morellon, Phys. Rev. B **69**, 144401 (2004).

[7] H. Kato, T. Okuda, Y. Okimoto, Y. Tomioka, K. Oikawa, T. Kamiyama, and Y. Tokura, Phys. Rev. B **69**, 184412 (2004).

[8] G. Popov, M. Greenblatt, and M. Croft, Phys. Rev. B **67**, 024406 (2003).

[9] D. Serrate, J. M. De Teresa, P. A. Algarabel, C. Marquina, L. Morellon, J. Blasco, and M. R. Ibarra, J. Magn. Magn. Mater. **290/291**, 843 (2005).

[10] Horng-Tay Jeng and G. Y. Guo, Phys. Rev. B **67**, 94438 (2003).

[11] Cz. Kapusta, D. Zając, P. C. Riedi, M. Sikora, C. J. Oates, J. Blasco, and M. R. Ibarra, J. Magn. Magn. Mater. **272-276**, e1619 (2004).

[12] H. Wu, Phys. Rev. B **64**, 125126 (2001).

[13] Z. Szotek, W. M. Temmerman, A. Svane, L. Petit, and H. Winter, Phys. Rev. B **68**, 104411 (2003).

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

[15] B. L. Henke, E. M. Gullikson, and J. C. Davis, At. Data Nucl. Data Tables **54**, 181 (1993) (available online: http://www-cxro.lbl.gov).

[16] H. Ebert, in *Spin-Orbit-Influenced Spectroscopies of Magnetic Solids*, Lecture Notes in Physics Vol. 466, edited by H. Ebert and G. Schütz (Springer, Berlin, 1996), p. 159.

[17] F. Wilhelm, P. Poulopoulos, H. Wende, A. Scherz, K. Baberschke, M. Angelakeris, N. K. Flevaris, and A. Rogalev, Phys. Rev. Lett. **87**, 207202 (2002).

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