Magnetization of Re-based double perovskites: Noninteger saturation magnetization disclosed

J. M. De Teresa, a) J. M. Michalik, J. Blasco, P. A. Algarabel, and M. R. Ibarra
Instituto de Ciencia de los Materiales de Aragón, CSIC-Universidad de Zaragoza, Zaragoza 50009, Spain

C. Kapusta
AGH, University of Science and Technology, 30-059 Cracow, Poland

U. Zeitler
High Field Magnet Laboratory, Radboud University Nijmegen, 6525 ED Nijmegen, The Netherlands

(Received 18 May 2007; accepted 31 May 2007; published online 21 June 2007)

Using static magnetic fields up to 30 T, the authors have measured the high-field magnetization in high-quality samples made from Re-based double perovskites: A2FeReO6 (A2=Ca2, Sr2, BaSr) and Sr2CrReO6, with Curie temperatures ranging from 360 up to 610 K. The results indicate that the saturation magnetization in these compounds is higher than the assumed spin-only ionic values, 3μB/f.u. for A2FeReO6 and 1μB/f.u. for Sr2CrReO6, which is explained by the large orbital contribution to the magnetization. Indirectly, these results show that Re-based double perovskites cannot be described as half-metals. © 2007 American Institute of Physics.

Half-metals are magnetic materials with carriers showing only one spin direction at the Fermi level, either parallel or antiparallel to the magnetization direction, and have a huge potential in the field of spin electronics. Ferromagnetic double perovskites (AB′B′′O6, A=alkaline earth metals and B′B′′=transition metals) have recently attracted great attention due to their presumed half-metallicity as well as high Curie temperature (TC). Thus, Sr2FeMoO6 (TC=420 K),1 Ca2FeReO6 (TC=520 K),2 Sr2CrReO6 (TC=610 K),3 and Sr2CrOsO6 (TC=720 K) (Ref. 4) are currently being actively studied with this purpose. A review article on these exciting materials was recently published.5

The A2FeReO6 (A2=Ca2, Sr2, Ba2) compounds were already studied in the past,6 way before the renewed interest in the light of applications for magnetoelectronics. In these compounds, it is generally assumed that five “localized” 3d electrons produced by Fe (S=5/2) will align antiparallelly to two “delocalized” electrons shared by Fe and Re and mediating a double-exchange-like interaction through the oxygen orbitals. Ideally, the conduction electrons will show complete negative spin polarization at the Fermi level, say, half-metallicity. Such an ionic picture implies an expected spin-only saturation magnetization (Ms) of 3μB/f.u. However, a number of striking features recently discovered in A2FeReO6 have clearly demonstrated that the physics of these compounds is much more challenging than previously assumed. First, the ground state has been found to change from metallic for A2=Ba2 to semiconducting for A2=Ca2,7 even though Ca2FeReO6 shows the highest TC in the series. An unexpected very large magnetic anisotropy was found and attributed to the intrinsic anisotropy of Re ions.8 Strong magnetostuctural effects have also been reported in this series by neutron diffraction,9 which are also nicely reflected in a large anisotropic magnetostriction totally unexpected in ferromagnetic oxides without orbital instabilities.10 The large spin-orbit coupling exhibited by the Re ions (5d element) in this series has been disclosed through x-ray magnetic circular dichroism (XMCD) measurements that show the presence of a significant orbital moment.11 With respect to the potentiality of these compounds for magnetoelectronic applications, the large intergrain magnetoresistance found in polycrystalline pellets suggested half-metallicity,12 even though this property has never been demonstrated. In this letter, we aim to disclose one of the standing controversialies on Re-based double perovskites, i.e., the saturation magnetization of these materials and, indirectly, important aspects of their physical properties such as the existence or not of half-metallicity.

The compounds studied in the present work, A2FeReO6 (A2=Ca2, Sr2, BaSr) and Sr2CrReO6, were “fresh” samples synthesized by solid-state reaction techniques, as described elsewhere.6,13 The selected samples have a low amount of antisite (AS) disorder defects in order to make the conclusion robust (AS is known to decrease magnetization).14 The amounts of AS are only 0.5% for BaSrFeReO6, 2% for Sr2FeReO6, and 0% for Ca2FeReO6, which give us the opportunity to investigate Ms in almost-AS-free samples. We have carried out magnetization studies in the temperature range of 300–700 K by means of an ADE Electronics EV7 vibrating sample magnetometer with the sensitivity of 10^-6 emu. As previously reported, TC for BaSrFeReO6, Sr2FeReO6, and Ca2FeReO6 is found to be, respectively, ≈360, ≈410, and ≈520 K.15 Magnetization isotherms above TC show the expected linear dependence with the magnetic field. From the extrapolation of the linear behavior onto the ordinate axis, the extrinsic magnetization caused by ferromagnetic impurities is estimated to be ≈0.065, ≈0.25, and ≈0.05 emu/g for BaSrFeReO6, Sr2FeReO6, and Ca2FeReO6, respectively. This corresponds, respectively, to 0.2%, 0.7%, and 0.1% of the saturation magnetization values of BaSrFeReO6, Sr2FeReO6, and Ca2FeReO6, which allow us to discard any relevant influence on the reported effects.

Magnetization measurements up to 5 T have been performed with a Quantum Design superconducting quantum interference device (SQUID) magnetometer with sensitivity ≈5×10^-7 emu. The magnetization values at 4 K under 5 T for BaSrFeReO6, Sr2FeReO6, and Ca2FeReO6 are, respec-

a)Author to whom correspondence should be addressed; electronic mail: detteresa@unizar.es
FIG. 1. (Color online) (a) Magnetization hysteresis loop at 4 K up to 30 T of BaSrFeReO$_6$. Bottom inset: zoom in of the magnetization in the vicinity of 30 T. The line marks the value expected for the saturation magnetization without orbital contribution to the magnetization. Top inset: comparison between the magnetization results obtained with SQUID up to 5 T (squares) and the results obtained in the high-field installation (line). (b) The same for Sr$_2$FeReO$_6$. (c) The same for Ca$_2$FeReO$_6$. (d) The same for Sr$_2$CrReO$_6$.

respectively, found to be 2.98μ$_B$/f.u., 2.81μ$_B$/f.u., and 2.25μ$_B$/f.u. Nevertheless, 5 T is not a sufficient field to saturate the magnetization. High-field magnetization measurements up to 30 T have been performed at the High Field Magnet Laboratory, Radboud University Nijmegen, Netherlands by using a Bitter coil. The magnetization is measured with the extraction method via two pick-up coils connected in series opposition. In Fig. 1(a) we show the magnetization hysteresis loop at 4 K up to 30 T of the BaSrFeReO$_6$ sample. Under the maximum field of 30 T the magnetization is found to be 3.27μ$_B$/f.u., much above the previously assumed value of 3μ$_B$/f.u. As can be noticed in the inset of this figure, this compound is almost saturated under 30 T. This fact, together with the small value of AS (0.5%), allows us to establish the value of 3.30(5)μ$_B$/f.u. for the $M_S$ of this compound if we use the expression $M_S$(exp)=$M_S$[(1−2)AS], where $M_S$(exp) is the measured experimental value and $M_S$ is the value without AS. This dependence of the saturation magnetization on AS has been used in the past in double perovskites, with good agreement with the experimental results.\textsuperscript{14,15} As shown in the inset of Fig. 1(a), at 100 K and under the maximum field of 30 T the magnetization is found to be 3.21μ$_B$/f.u., still much above 3μ$_B$/f.u. The slight increase of the magnetization between 100 and 4 K [see the inset of Fig. 1(a)] also allows us to discard any kind of spurious paramagnetic signal that could contribute to the measurement at 4 K. The measurements on Sr$_2$FeReO$_6$ are shown in Fig. 1(b). Similar conclusions can be drawn for this compound. In this case, under the maximum field of 30 T the magnetization is found to be 3.23μ$_B$/f.u. at 4 K and 3.17μ$_B$/f.u. at 100 K. However, in this compound the tendency to saturate is less clear than for BaSrFeReO$_6$, and it seems that a few more tesla are required to achieve saturation. Taking into account the level of antisites in this sample, one can estimate the $M_S$ of this compound to be 3.33(5)μ$_B$/f.u. by using the expression introduced before. This is indeed only an approximate value due to the lack of complete magnetic saturation at 30 T. The lack of magnetic saturation under 30 T is evident in the Ca$_2$FeReO$_6$ sample, whose results are shown in Fig. 1(c). Under the maximum field of 30 T the magnetization is found to be around 3.12μ$_B$/f.u. at 4 and 100 K. We ascribe the lack of increase of the $M_S$ in the temperature range between 100 and 4 K to the fact that a structural transition between two monoclinic crystallographic structures takes place in this compound below 120 K.\textsuperscript{7,8} The lack of magnetic saturation at 30 T in this compound prevents us from establishing an
For the sake of completeness, we include in this letter the results obtained during these experiments in another important Re-based double perovskite, Sr$_2$CrReO$_6$, with a high half-metallicity at the Fermi level. The existence of noninteger saturation magnetization suggests that Re-based double perovskites are not half-metals, as previously assumed. Nevertheless, for Sr$_2$CrReO$_6$ it has been calculated that the carriers at the Fermi level remain highly polarized (>90%) (Ref. 19) and could still be very attractive for applications in spin electronics.

The authors acknowledge financial support by Project Nos. MAT2005-05565-C02-02 (MECD, Spain) and EuroMagNET-RII3-CT-2004-506239 (6FP, EU) and are grateful to R. Córdoba and D. Serrate.