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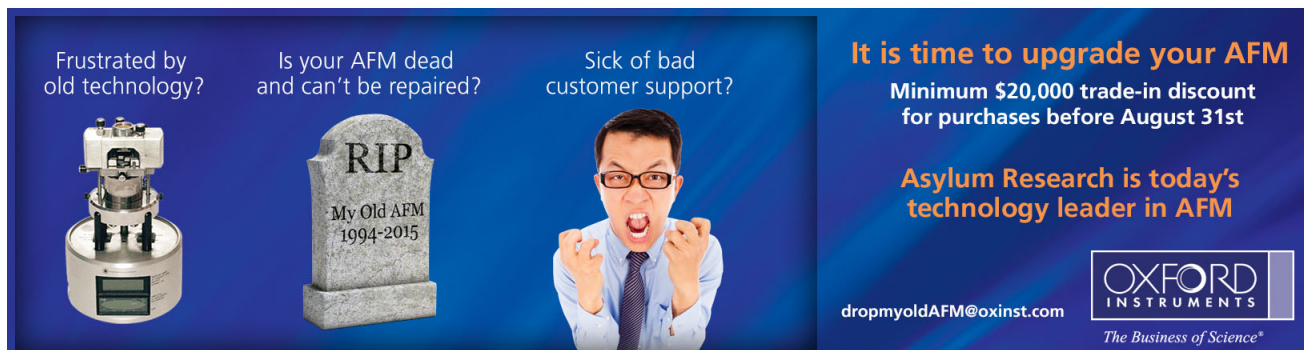Magnetic moment investigations of epitaxial magnetite thin films
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Investigation of the local Fe magnetic moments at the grain boundaries of the Ca$_2$FeReO$_6$ double perovskite

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The local Fe ferromagnetic (FM) moment at the grain boundaries of a ceramic sample of Ca$_2$FeReO$_6$ double perovskite was investigated by means of x-ray magnetic circular dichroism spectroscopy at the Fe $L_{2,3}$ edges and compared to the overall bulk magnetization. We found that, at the grain boundaries, the Fe FM moments at $H=5$ T are much smaller than expected and that the $M \times H$ curve is harder than in the bulk magnetization. These results suggest a larger degree of Fe/Re antisite disorder at the grain boundaries of this sample, shedding light into the intriguing nonmetallic resistivity behavior despite the reported presence of free carriers. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2714317]

Double perovskites with formula A_2Fe(Mo,Re)O$_6$ (A =Ca,Sr,Ba) have recently attracted attention due to their interesting electronic and magnetic properties (for a recent review, see Ref. 1). Most compounds of the family present large tunneling magnetoresistance at room temperature,[2–7] which has been associated with half-metallic electronic band structures.[2,3,8–13] Such behavior is closely related to the ferrimagnetic alignment of Fe and (Mo,Re) spins. In fact, due to this magnetic structure, the Mo (Re) $4d$ ($5d$) down spin electrons may hop to the $3d$ empty levels of neighboring Fe ions, leading to the half-metallicity. Nonetheless, the electronic properties of the compound Ca$_2$FeReO$_6$ (CFRO) appear to contrast with the general behavior of the family. Resistivity of ceramic samples shows a nonmetallic behavior for all temperatures,[4,14,15] while an infrared study revealed the presence of free carriers above a metal-insulator transition at $T_{MI} \sim 150$K, and the opening of a gap below T_{MI}.[14,16] Such nonmetallic behavior has not been captured by band structure calculations.[10,11] Strong correlation effects of the Re $5d$ electrons have been suggested.[17,18] The ferrimagnetic-to-paramagnetic transition temperature is rather large, T_C $\sim 521–539$ K.[17,19–22] Also, this compound appears to be magnetically harder than similar materials,[20] and other intriguing effects such as a positive magnetoresistance at low temperatures have been found.[23] The large T_C and the intriguing magnetotransport behavior of CFRO suggest that elucidating the magnetism of this compound may pave the way for a better understanding of the physics of all the members of the family. A relevant ingredient for the physics of the A_2FeReO$_6$ family is the very large Re orbital moment in this material, which has been directly demonstrated for A=Ca

(Ref. 24) and A=Ba.[25] In this work, we investigate the local Fe magnetism at the grain boundaries of CFRO by means of x-ray magnetic circular dichroism (XMCD) measurements at the Fe $L_{2,3}$ edges as a function of T and H, and compare our findings to the bulk magnetization behavior.

The polycrystalline sample CFRO was synthesized by high temperature solid state reaction in sealed evacuated silica tubes at 910 °C. Accordingly, the grain sizes are expected to be in the micrometric scale. In fact, a previous neutron diffraction study on the same sample indicate crystalline domains larger than 0.1 μm.[17] More details of preparation procedures and characterization of the sample used in this work are described in Refs. 4 and 5. The XMCD measurements were done in the total electron yield mode measuring the drain current in the sample on the high field magnet end station, at the beamline ID08 of the European Synchrotron Radiation Facility (ESRF). A fresh piece of the sample with platelike shape was chosen. The sample was glued on aluminum plates with silver epoxy and mounted so that the flat face normal was antiparallel to the direction of the incident beam. Once in the preparation chamber, the sample was diamond filed in order to obtain a uniform clean surface. The sample was then transferred to the superconducting magnet just after scraping, where they remained under a pressure of around 5×10^{-10} mbar during measurements. The incident intensity of the beam was measured by means of a gold grid far away enough to avoid interference from the high magnetic field. The circular polarization degree of the beam was always $\sim 100\%$ and the calculated energy resolution at Fe $L_{2,3}$ edges is 0.2 eV. The experimental dichroic signal was obtained by the subtraction of the spectra with the orientation of photon helicity parallel to the sample magnetization from the spectra obtained with the orientation of helicity antiparallel to the sample magnetization.

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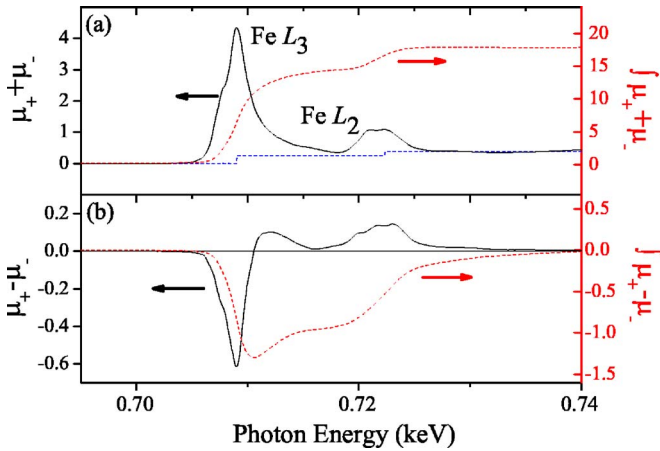a)Electronic mail: azimonte@ifi.unicamp.br

FIG. 1. (Color online) The XAS ($\mu_+ + \mu_-$) and XMCD ($\mu_+ - \mu_-$) spectra at the Fe $L_{2,3}$ edges for Ca_2FeReO_6 at $T=10$ K and $H=5$ T (solid lines). The edge jump is given in (a) as blue (dark gray) dashed lines. The dotted lines in red (gray) in (a) and (b) indicate the XAS and XMCD integration, respectively.

The data were taken by alternating between two opposite directions of the magnet (H^+ and H^-). For each direction of the magnetic field, four spectra were measured following the sequence σ^+, σ^-, σ^-, σ^+, in order to minimize systematic errors. The x-ray absorption spectroscopy (XAS) spectra is used as the sum of the absorption spectra in both directions (σ^+ and σ^-). dc magnetization measurements were performed with a superconducting quantum interference device magnetometer using the same thermomagnetic history and sample geometry with respect to the field as in the XMCD measurements, in order to equalize the geometrical demagnetization factor and other possible extrinsic effects in both measurements.

Figures 1(a) and 1(b) show the XAS spectra and the dichroic signal (XMCD) of CFRO at the Fe $L_{2,3}$ edges at $T=10$ K and $H=5$ T. The XAS integration was made after edge-jump removal. Surprisingly, the XAS spectrum is not characteristic of single-valent Fe^{3+} in a perovskite structure,[26] despite a previous estimation of an Fe valence close to +3 by bond-valence analysis[17] and Mössbauer experiments[5] on the same sample used in this work. Instead, the XAS spectrum of CFRO is similar to that of Fe_3O_4 with an average Fe valence of +2.67 (see Ref. 27). On the other hand, the Fe local atomic environment is not equivalent in CFRO and spinel Fe_3O_4, and therefore their XAS spectra cannot be trivially compared in order to safely extract the formal Fe valence in CFRO. A more quantitative analysis of the formal Fe valence state in CFRO is beyond the scope of the present work. Nonetheless, it can be safely stated at this point that such state is closer to Fe^{3+} than Fe^{2+}. The Fe spin and orbital magnetic moments were then calculated using the well-known sum rules for XMCD,[28,29] using the calculated Fe 3d electron occupation number of 5.84,[10] neglecting the expectation value of the dipole operator,[30] and applying the correction term $1/0.685$ due to the spin-orbit coupling in the $Fe^{3+} 2p$ core holes.[25,31] Using a different correction term due to a possible fraction of Fe^{2+} ions might slightly reduce the estimated $M_{spin}(Fe)$ given below (by less than 10%). The obtained moments at $T=10$ K and $H=5$ T
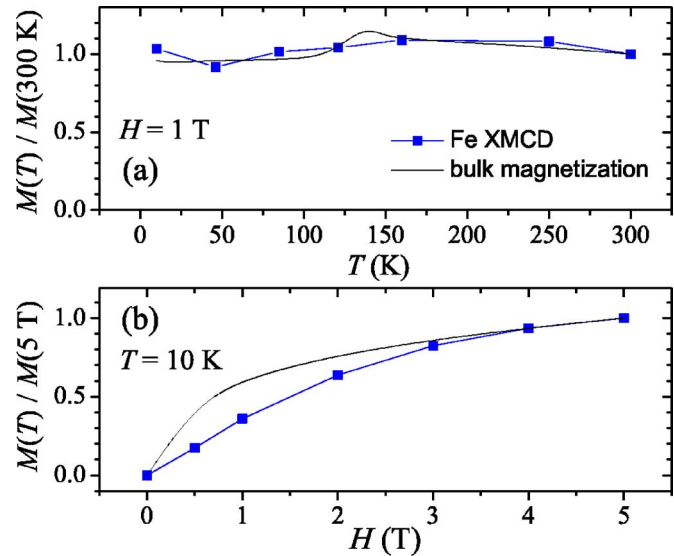

FIG. 2. (Color online) Bulk magnetization (solid line) and Fe magnetic moment at the grain boundaries obtained from our XMCD analysis (filled squares, see text) as a function of (a) temperature for $H=1$ T and (b) applied magnetic field for $T=10$ K. The measurements in (a) and (b) were normalized by the values at 300 K and at 5 T, respectively.

were $M_{spin}(Fe)=1.95(15)\mu_B$, $M_{orb}(Fe)=0.00(2)\mu_B$, and $M_{total}(Fe)=1.95(15)\mu_B$, much smaller than the bulk value of $M(Fe)=3.42(7)\mu_B$ obtained by neutrons.[17]

Figures 2(a) and 2(b) show $M_{total}(Fe)(T)$ for $H=1$ T and $M_{total}(Fe)(H)$ for $T=10$ K, respectively, compared to the overall bulk magnetization behavior of CFRO measured by magnetometry under the same conditions. The bulk magnetization was taken for opposite directions of magnetic field at each point in order to simulate the same thermomagnetic history as in the XMCD measurements. A similar behavior of bulk and XMCD results might, in principle, be expected for a homogeneous sample, since the Fe moments, being much larger than the Re moments,[17] dominate the overall magnetization. Nonetheless, while the T dependent Fe moments at 5 T are indeed consistent with the overall bulk magnetization behavior within our accuracy, the H dependency of $M_{total}(Fe)$ measured by XMCD at 10 K shows a largely different behavior with respect to the bulk magnetization, the $M \times H$ curve being clearly magnetically harder in the XMCD measurements.

The largely distinct behavior between the overall magnetization and our XMCD results is related to the surface sensitivity of the latter technique in total electron yield mode (of the order of 50 Å), in contrast to the magnetometry technique. Thus, our results allow for a comparison between the bulk magnetic behavior with that of the grain boundaries of our CFRO ceramic sample. It is interesting to note that a detailed magnetotransport investigation in this and related compounds revealed magnetoresistance peaks at larger fields than the coercive one, contrary to what is expected for an intergrain magnetoresistance mechanism.[23] To rationalize this result, it was assumed that the grain surface is magnetically harder than the bulk.[23] In fact, the result of Fig. 2(b) confirms such a hypothesis.

It is valid to ask the reason why the grain surface is magnetically harder than the core. A plausible explanation might be related to a possibly larger degree of antisite disorder between the Fe and Re ions at the grain surface. In this scenario, and assuming that the Fe spins occupying the Re site would align in the direction of the Re moments, i.e., antiparallel to the main Fe sublattice, the FM Fe moment obtained by XMCD would be reduced, accounting for the much lower Fe magnetization at 5 T obtained by XMCD than the neutron results at zero field (see above). Under the application of even stronger magnetic fields, these antisite moments would tend to align with the field and therefore with the main Fe sublattice, possibly leading to an increase of the Fe moment obtained by XMCD towards the bulk value obtained by neutrons.

The above scenario may be used to rationalize the non-metallic behavior of CFRO obtained by resistivity measurements over the whole temperature range,[4,14] in spite of the presence of free carriers revealed by infrared measurements.[14] In fact, atomically disordered regions tend to favor carrier localization, and it is reasonable to consider that the grain boundaries may act as a potential barrier for the conduction electrons. The conduction process would then arise from an insulating component due to the intergrain hopping in the presence of a disordered boundary, in series with a metallic component due to the intragrain transport behavior. This would result in an overall nonmetallic behavior for the resistivity, in spite of the presence of free carriers, such as observed experimentally above T_{MI}.[4,14]

In conclusion, a comparison between Fe $L_{2,3}$ edge XMCD and bulk magnetization results in CFRO indicates that the grain boundaries are magnetically harder than the grain core. A larger degree of antisite disorder in the boundaries was suggested, providing a plausible explanation for the nonmetallic resistivity observed in this compound, even in the presence of free charge carriers.

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