ESRF	**Experiment title:** HALF METALLIC CHARACTER OF DOUBLE PEROVSKITES THIN FILMS A2B'B''O6 (B' = Fe; B'' = Mo, Re) PROBED BY SELECTIVE XMCD AT BOTH TRANSITION METALS L₂,₃ EDGES	**Experiment number**: HE 848-HE 865
Beamline: ID 12 and ID8	**Date of experiment**: from: 06/12/00 to: 12/12/00 from: 11/04/01 to 17/04/00	**Date of report**:
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Report:

The double perovskites $A_2B'B''O_6$ (where A = Ca, Sr, Ba and B'B''=FeMo, FeRe, FeCr, CrMo…) are among the most promising materials for integration in the next generation of spintronic devices because of a predicted 100% spin polarization combined with Curie temperature (T_C) above room temperature. For instance, recent experiments on Sr_2FeMoO_6 [1] predict by band structure calculations and magnetoresistance in polycrystalline samples the half-metallic nature of its ground state and a Curie temperature of around 450 K, which could allow excellent performance for applications at room temperature. A simple picture to explain the magnetic and electronic properties of those new materials is that a spin of S = 5/2 is localized on the Fe site, while the Mo $4d$ t_{2g} (S = 1/2) electron is strongly hybridized to the Fe $3d$ t_{2g} electrons via the oxygen states. In that case, the antiferromagnetic superexchange interaction between the two magnetic ions should occur. The aim of this project was to perform XMCD measurements at the $L_{2,3}$ edges on both transition metals (B site) of each compound to get a better understanding of the properties of the double perovskite materials.

The XMCD experiments were carried out on two ESRF beamlines : IB 12 for the experiments at the Mo $L_{2,3}$ edges and on IB 08 for the Fe $L_{2,3}$ edges and O K edge. The measurements have been performed at 40 K under a magnetic field of ±5 Tesla. The dichroism signal have been obtained either by changing the phase at fixed magnetic field or changing the applied field direction for a fixed polarisation. The studied samples are thin films of Sr_2FeMoO_6, bulk single crystal of Sr_2FeMoO_6 and a serie of polycrystalline bulk targets (obtained by solid state reaction) of $Sr_{2-x}La_xFeMoO_6$ in order to link the increase of the Curie Temperature induced the La substitution to modifications of the magnetic moments of both Fe and Mo elements.

First, we have obtained very nice results on the magnetic structure of a Sr_2FeMoO_6 single crystal which is still controversal. In fact, in all the proposed model, the basic requirements for half metallicity are the existence of a finite magnetic polarization of the non magnetic Mo ions aligned oppositely to Fe moment and also the high spin (S=5/2) arrangement of the five other d electrons localized on the Fe site, that is a strong

intra-atomic ferromagnetic exchange compared to the crystal field separating the t_{2g} and e_g energy levels in octahedral sites. Any deviation from these conditions could induce a Fe low spin destroying the half metallicity. Nevertheless, on the experimental side, serious controversies remain. One of them is the value or even the existence of the spin magnetic moment at the Mo site obtained by different techniques. While previous X-ray magnetic circular dichroism (XMCD) by Ray et al[2] do not yield any observable spin magnetic moment on Mo in agreement with neutron diffraction[3], the same neutron technique[4] revealed a moment close to 1 μ_B. Another discrepancy concerns the valency of Fe: on one hand, by X-ray absorption spectroscopy (XAS) with linear polarized light, Ray et al conclude that Fe is in the 3+ state. On the other hand Mossbauer spectroscopy data either agree with this value [5] or establish that Fe is in a $Fe^{2.5+}$ state[6]. Consequently, these contradictory observations question the mechanism responsible for both the coupling and the conduction and thus indirectly the reality of the half metallicity of SFMO. We have obtained on a Sr2FeMoO6 single crystal from our XMCD measurements at the $L_{2,3}$ edges of Fe and Mo sites, spin moments of +3.05 and -0.32 μ_B for Fe and Mo, respectively, and no significant orbital. A total magnetic moment of 2.85μB per Fe-Mo pair, deduced from dichroism measurements, is fairly close to the macroscopic magnetization of 3.2 μ_B obtained by SQUID magnetometry. For the first time, a direct proof of the antiferromagnetic interaction between both sublattices is given by the respective signs of the dichroic signal. Also, the calculated proportion of 66% of Fe^{2+} and 34% of Fe^{3+} is in good agreement with the spin moment measured on Mo sites. All this evidence seems to confirm, consistently with our LSD-SIC calculations, that a localized spin carried on Fe sites and a delocalized electron of Mo are responsible for the half metallicity of this compound. This part of our work has been submitted to EuroPhysics Letters.

Concerning the Sr_2FeMoO_6 thin films, we would like to emphasize that a strong effort was made prior to the experiment to prepare and characterize the best films compared to the state-of-the-art (cf M. Besse et al, *Suitable methods to identify epitaxial Sr_2FeMoO_6 thin films,* to be published in J. Crystal Growth). We were able to detect (by fluorescence) a significant Mo magnetic moments (about 0.25 μ_B/atom), thus fullfilling, as pointed before, one of the basic requirements for half metallicity. However the results at the Fe edges on the thin films were disapointing (both the XAS and the XMCD spectra were strongly different from those taken on the single cristal). The main reason to explain these differences is that the thin films (100 nm thick) were not covered because we did not identify at that time a protecting material that do not modify the structural properties of the Sr_2FeMoO_6 thin films. Keeping in mind that we have used a surface sensitive detection method (total electron yield), we can conclude that even if the bulk of the films has probably the good properties, the structural and the electronic properties at the external interface are strongly modified and thus the half metallic character is lost.

For the La substituted $Sr_{2-x}La_xFeMoO_6$ bulk samples, we clearly observed that increasing the substitution induces a reduction of the spin moment borne by the Fe atoms, whereas the Mo magnetic moment increases (up to x = 0.6). Our explanations are that the supplementary electrons brought in the system by the La atoms are distributed on both Fe and Mo sites. Taking the hypothesis that the band structure is not strongly modified by the substitution (valid for small x values), theses electrons shift the Fermi level. In such case, on the Fe sites, it would lead to a gradual filling of the t_{2g} and e_g spin down orbitals because the spin up ones are already full and thus induces a reduction of the Fe magnetic moment. On the contrary, on the Mo site, the filling of the t_{2g} down orbital by the supplementary electrons increases first the Mo magnetic. For larger La subtitution (x > 0.6), we found that both Fe and Mo magnetic moments drastically decrease. This is most probably due to the appearance of structural modifications (site disorder, parasite phases etc…). These results are the first step in the understanding of how to tune optimally the magnetic properties of double perovskites materials "playing" with the number of electrons participating to the conduction.

References :

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