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ESRF

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 12A for the experiments at the Mo $L_{2,3}$ edges and on IB 12B 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 polycrystalline bulk targets (obtained by solid state reaction) of FeMo based double perovskites with different lanthanide atoms, resp. Ca, Sr and Ba. The different lattice parameter induce substantial modifications of the T_C found in the corresponding compounds. Although Sr_2FeMoO_6 is the most promising candidate in terms of applications because of its high Tc ($\approx$ 450 K), we were interested in the study of the size effect on the magnetism and the conduction mechanisms due to the structural modification of the three materials.
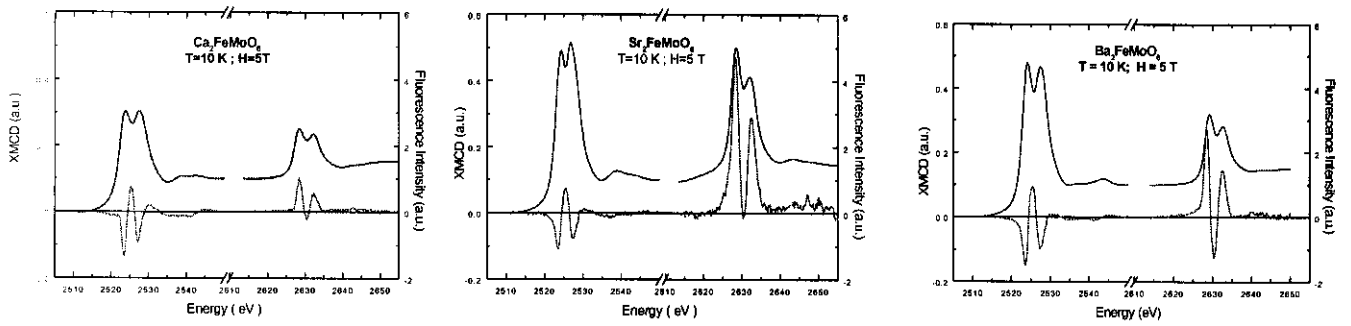
Fig. 1 : Absorption and XMCD at the Mo $L_{2,3}$ edges on Ca_2FeMoO_6, Sr_2FeMoO_6, Ba_2FeMoO_6 polycrystalline bulk samples

On Fig 1, we show the absorption spectra and the dichroism signal at the Mo $L_{2,3}$ edges for Ca_2FeMoO_6, Sr_2FeMoO_6 and Ba_2FeMoO_6. We have also measured (not shown) as reference samples the absorption spectra on various Mo ionic compounds (K_2MoO_4, $K_{0.3}MoO_3$, MoO_3,) and a metallic Mo foil. Clear differences are observable between the three absorption curves on the $L_{2,3}$ integrated area as well as on the intensity ratio of the doublet peaks observed at each absorption edge. All these features should be linked to modifications of the electronic properties related to size effect. However we could not discern only by comparison with the reference samples the exact valence state for each materials. Within the intuitive view proposed by Tokura et al for Sr_2FeMoO_6, the Mo magnetic moment should be less than 1 µB/atom because of the itinerant character of the $4d$ t_{2g} electron. Applying the sum rules (taking 0.5 holes in the Mo $4d$ band), we estimate a total Mo magnetic moment equal to 0.3 μ_B for CFMO, 0.7 μ_B for SFMO and 0.4 μ_B for BFMO with 10% error bars. The value measured for SFMO is higher than the one calculated by Tokura et al (0.29 μ_B). By the way, these measurements are the first XMCD experiments at the energy of Mo $L_{2,3}$ edges despite the low circular polarisation (4-10%).

Fig 2 displays the absorption spectra and the dichroism signal at the Fe $L_{2,3}$ edges in Sr_2FeMoO_6. Concerning the two others materials, the absorption curves look very similar whereas the dichroism signal slightly differ from the one of Sr_2FeMoO_6. We have evaluated the ratio : absorption per $3d$ Fe holes from the XMCD on a Fe reference sample. Injecting that quantity in the sum rules, we estimated for example that the magnetic moment carried by the Fe atoms is about 3.3 μ_B in Sr_2FeMoO_6 and similar results for the other samples. Respect to the magnetic configuration of the two magnetic sites in the double perovskites, we found in Sr_2FeMoO_6 that the magnetic moment on Fe and Mo are antiparallel in agreement with the picture of a superexchange interaction between the $3d^5$ and $4d^1$ spins. This is not the case for Ca_2FeMoO_6, Ba_2FeMoO_6 in which the magnetic moments are coupled ferromagnetically. We might suppose that in those cases the 5 Tesla applied

Fig.2 : Absorption and XMCD at the Fe $L_{2,3}$ edges on Sr_2FeMoO_6 polycrystalline bulk samples measured at 10K with an applied field of ± 5 Tesla.

magnetic field is strong enough to act against the antiferromagnetic interaction. A field dependence study would be necessary to clear out this point. However in all cases, we always found a magnetic moment per formula unit lower than the 4 μ_B which the expected value for the generally accepted picture of an ideal ferrimagnetic arrangement in a pure ionic model.
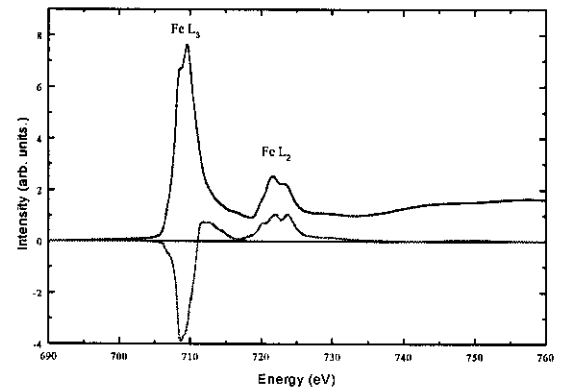
To summarize, we have been able to measure separatelly the magnetic and electronic properties of Fe and Mo in FeMo double perovskites. From a first analysis, we can clearly observe some modifications in the results because of the size effect induced by the different lattice parameters of the lanthanides atoms. It seems also clearly that one has to go beyond the general ideas which are proposed up to now to identify the actual mechanisms governing both the magnetism and the conduction in these compounds. We are currently in contact with theoristicians in order to perform some atomic multiplet calculations which should help us to better understand our results and thus answer more precisely all the opened questions on the magnetic and electronic properties of the double perovskites.