ESRF	**Experiment title: Hard X-ray RIXS-MCD investigation of binary ferrofluids**	**Experiment number**: HE-1266
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Shifts: 18	**Local contact(s)**: Dr. Mauro Rovezzi	*Received at ESRF:*

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Report:

The goal of this proposal was to study, for the first time, magnetic couplings and local anisotropies in analogues of binary ferrofluids (i.e. colloidal suspensions of ferrite nanoparticles) using the newly developed RIXS-MCD spectroscopy. Initially, we had planned to investigate, as a first step, quenched analogues of binary ferrofluids, i.e. ferrofluids whose structure has been quenched by dispersing nanoparticles in a silica matrix, instead of a liquid. Meantime, our collaborators in PHENIX laboratory in Paris managed to obtain ferrofluid samples of excellent quality (in terms of monodispersity, size, and composition). Hence we decided that it was worth measuring directly on the liquid samples. Nevertheless this made necessary the design and development of a special sample holder that could deal with the different experimental constraints of such RIXS-MCD measurements: (i) the sample is in liquid phase at room temperature, (ii) the magnetic field (1.5 T) is generated by electromagnet with only 2 cm between the poles, (iii) incident beam is at 45° with respect to sample surface, (iv) detection is measured at 90° on the spectrometer, (v) room and low temperature measurements shall be done using the same setup in a Helium cooled cryostat.

The "sample environement group" of the ESRF developped the appropriate liquid cell in close collaboration with us and M. Rovezzi (ID26). The RIXS-MCD measurements were performed at room temperature using an electromagnet magnet positioned along the beam which can reach 1.5 T. We devoted a special care to minimize the systematic errors due to asymmetry in circular polarization degree for left and right handed photons. Hence RIXS-MCD measurements were repeated twice – once for each orientation of the magnetization (positive or negative) with respect to the incoming photons directions. This procedure was certainly shift-consuming, but in such a way we could obtain data of very good quality and reliability. To give an idea, the measurement of one RIXS-MCD plane required about 1 shift. Furthermore, none of these compounds had been investigated in liquid phase with RIXS / RIXS-MCD before. Hence it was necessary to investigate their stability under the x-ray beam and also to optimize the count rate. We have also measured HERFD and HEFD-MCD spectra in the edge region.

We first measured the RIXS-MCD signal on two reference samples: a $CoFe_2O_4$ ferrofluid (nanoparticles with diameter of 5.9 nm dispersed in heptane, Co K edge) and a $MnFe_2O_4$ ferrofluid (nanoparticles with diameter of 5.9 nm dispersed in heptane, Mn K edge). For both systems, the RIXS-MCD plane was measured at room temperature (liquid phase) and at ~25 K (frozen phase). At the Mn K pre-edge, the RIXS-MCD plane measured $MnFe_2O_4$ at 27 K (Figure 1) shows mainly a double (positive + negative) intense MCD feature (~17% peak to peak with respect to the

pre-dge maximum), which is consistent with a dominant contribution of tetrahedral Mn^{2+} . The data measured at the Co K pre-edge on $CoFe_2O_4$ particles are consistent with data previsouly measured on bulk ferrite samples by RIXS-MCD. The detailed and quantitative interpretation of the data measured for both samples, using Ligand Field Multiplet calculations, is under progress.

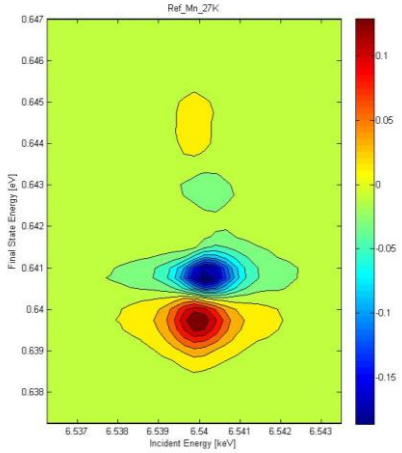

Figure 1. RIXS-MCD plane measured at T = 27K on the reference samples of $MnFe_2O_4$ (Mn edge) ferrofluid.

We have measured hysteresis loops detected by RIXS-MCD on both reference compounds, i.e. $CoFe_2O_4$ and $MnFe_2O_4$. These element selective magnetization curves (Figure 2) were measured at both room temperature and low temperature (i.e. below the solidification temperature of the solvant). Both incident energy and emission energy were first tuned to to the maximum of the RIXS-MCD signal in the pre-edge region and then the magnetic field was varied between -1.5T and 1.5T. The coercivity measured for the $CoFe_2O_4$ particles at the Co edge is on the order of 0.31 T at T=27K, while it is 0.013T for the $MnFe_2O_4$ particles at the Mn edge. At low temperature the measurement of a magnetization curve with a good signal to noise ratio (= the average of ten curves) requires about 2 hours.

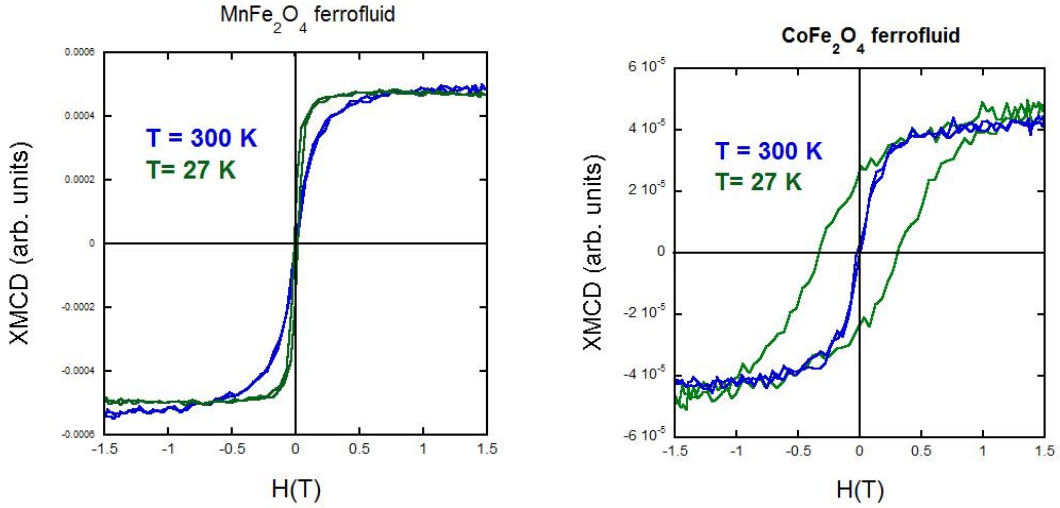

Figure 2. Hysteresis loops measured by RIXS-MCD on the reference samples of $MnFe_2O_4$ (left) and $CoFe_2O_4$ (right) ferrofluid at room temperature and at T=27K (average of ten magnetization curves).

Finally we have measured RIXS, RIXS-MCD and element selective magnetization curves on a binary ferrofluid which is a mixture of both reference ferrofluids. A first analysis of the results seems to indicate that magnetic anisotropies in the binary ferrofluid cannot be understood from a weighted superposition of both individual components. Further analysis of the data, together with TEM and SQUID data measured on the same samples, will allow to understand the magnetic properties of the binary sample.

The results obtained during this beamtime were / will be presented during several conferences:

- A. Juhin et al. 1st Meeting of the EUSPEC COST Action (Louvain la Neuve, Sept. 2015) – Invited talk
- N. Daffé et al. SOLEIL Users' Meeting 2015 (Saint Aubin, Feb. 2015)- Poster
- Two abstracts have been submitted to XAFS16 Conference (Karlsruhe, August 2015) : A. Juhin et al., N. Daffé et al.