ESRF	**Experiment title:** X-RAY MAGNETOCHIRAL DICHROISM (XMχD) OF RESOLVED ENANTIOMORPHOUS MOLECULAR MAGNETS	**Experiment number**: HE-1246
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1. AIM OF THE PROJECT

X-ray Magnetochiral Dichroism (XMχD) is new type of dichroism[1-3] which is related to non-reciprocal Optical Activity in systems in which not only ***Parity*** (I) but also ***Time-reversal*** (Θ) symmetries are broken. Recently, XMχD was observed[2] unambiguouly by the ESRF ID12 team in the low temperature phase of a well known magnetoelectric, ***Antiferromagnetic*** crystal of Cr_2O_3. Clearly, space Parity is broken in a resolved enantiomorphous (chiral) molecular magnet and, below the Curie Temperature (T_c) , Time-reversal symmetry should also be broken since such a molecular magnet is becoming ***ferromagnetic***. It was the aim of this project to investigate whether XMχD spectra could also be recorded below the Curie temperature in resolved enantiomers of chiral molecular magnets.

2. EXPERIMENTS

Under the leadership of Prof. M. Verdaguer, the partners of this project located at the Université P. & M. Curie (Université Paris VI) have gained an international reputation for the synthesis of novel and exotic molecular magnets. In this tentative project, we decided to concentrate first our efforts on the investigation of 2D bimetallic oxalate polymeric networks of the type $\{[M^{II}\,Cr^{III}\,(C_2O_4)_3][Fc\,CH_2NBu_3]\}_n$ obtained with chemically ***resolved*** (Δ) or (Λ) absolute configurations of the chiral $[Cr\,(C_2O_3)_3\,]^{3-}$ anions[4]. For 2D polymers with M = Mn, the Curie temperature is rather low (T_c = 5.3K) with a saturation magnetization of 7.2μ_B ; For M = Ni, the Curie temperature could be increased to 16K for a saturation magnetization of 4μ_B and a coercitive field of 0.2T. Unfortunately, no large size single crystal could be grown and all X-ray dichroim measurements had to be carried out with ***powdered*** samples.

We tried to record the following X-ray dichroism spectra in the Fluorescence mode at the Cr K-edge:

XMCD $\Rightarrow$ $[F(I_0^{(L)}, H\uparrow) - F(I_0^{(L)}, H\downarrow)] = [F(I_0^{(R)}, H\downarrow) - F(I_0^{(R)}, H\uparrow)]$

XNCD $\Rightarrow$ $\{[F(I_0^{(L)}, H\uparrow) - F(I_0^{(R)}, H\uparrow)] + [F(I_0^{(L)}, H\downarrow) - F(I_0^{(R)}, H\downarrow)]\}/2$

XMχD $\Rightarrow$ $\{[F(I_0^{(L)}, H\uparrow) + F(I_0^{(R)}, H\uparrow)] - [F(I_0^{(L)}, H\downarrow) + F(I_0^{(R)}, H\downarrow)]\}/2$

Unfortunately, we experienced serious problems due to dramatic radiation damages to the chiral oxalate moieties: we (finally) renounced to use our standard undulator HU-52 and we found much preferable to use the weaker 2nd harmonic of the low power hybrid undulator EMPHU; for the same reasons, the experiences were scheduled during runs in low current 16-bunches mode. Since we found that the rate of radiation damage was nearly constant with time, we elaborated an algorithm which allowed us to minimize the effects on our dichroism spectra.

3. RESULTS

Within our experimental error bars, we ***failed*** to detect any reliable XMχD signal whereas, as illustrated by Fig. 1, we succeeded in measuring high quality XMCD and XNCD spectra. Typically, the XNCD spectra had opposite signs for the two enantiomers whereas the corresponding signal vanished in the case of the racemic molecular magnet. The detection of XNCD spectra was rather unexpected because the E1E2 interference terms are expected to vanish in a powdered sample whereas the contribution of E1M1 terms is strongly forbidden by selection rules. Our experiment seem to prove that the ***orientational isotropy*** of space is lost in the powdered samples due to the ferromagnetic order. High quality XMCD spectra were recorded although the signal is known to be rather small at any K-edge. Most typical is the observation of a strong multi-electron signal near 6042 eV: this signal is real and could even be used to obtain the magnetization curve displayed in Fig. 2. More work would still be desirable in order to clarify why no XMχD signal was detected in these systems.

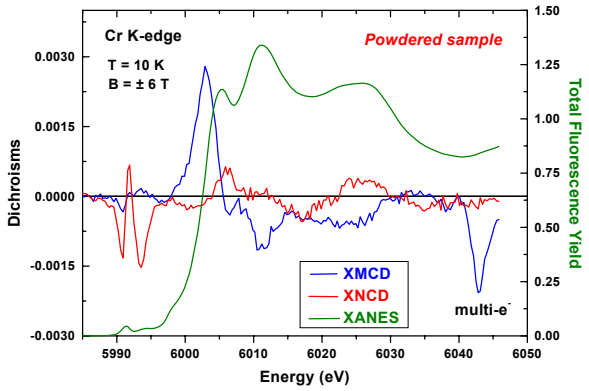

Figure 1

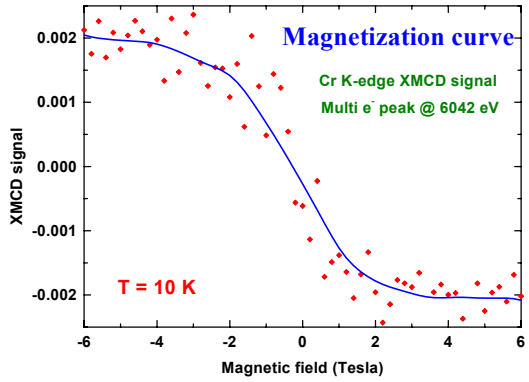

Figure 2

References

[1]J. Goulon *et al. PRL* **88** (2002), 237401-1

[2]J. Goulon *et al. J. Phys.: Condens. Matt.* **15** (2003), S633.

[3]J. Goulon *et al. JETP* in press (2003), S633.

[4]R. Andres *et al. Inorg. Chem.* **40** (2001), 4633.