ESRF	Experiment title: Interplay between structural chirality and magnetism in Mn and Co-based Single Chain Magnets	Experiment number: HE-3911
Beamline:	Date of experiment:	Date of report:
ID12	from: 23/10/2012 to: 30/10/2012	28/01/2012
Shifts: 18	Local contact(s): Andrei Rogalev	Received at ESRF:
Names and affiliations of applicants (* indicates experimentalists):		
Roberta Sessoli*, Matteo Mannini*, Andrea Caneschi, Marie-Emmanuelle Boulon*, Lorenzo Poggini*		
Laboratory for Molecular Magnetism, Dip. Chimica "Ugo Schiff" and INSTM Ru of Firenze, Italy		
A $a_1 a_2$ D $a_2 a_1 a_2$ ψ D $a_1 a_2 a_3$ W/11 $a_1 a_2 \psi$		

Andrei Rogalev*, Fabrice Wilhelm*

ESRF Synchrotron, ID12 beamline, Grenoble (France)

Report:

Chirality and magnetism are directly connected in the interaction between matter and electromagnetic radiation through the magneto-chiral dichroism and birefringence,^{1, 2} which was observed for the first time relatively recently by Rikken & Raupach³ and even more recently using X-ray radiation.⁴ Magneto-chiral dischroism (M χ D), i.e. the different absorption of unpolarized light by systems with opposite chirality in the presence of a magnetic field, is a fascinating phenomenon that has been suggested to be a the origin of homochirality of life on the earth. It is in general very weak, being assumed in first approximation to be related to the product of natural (NCD) and magnetic circular (MCD) dichroism, and only few examples are available in the literature. No systematic experimental studies to investigate which are the factors that originate the phenomenon are available.

During this beamtime (HE-3911) we have investigated the X-edge of Mn and Co on two isostructural molecular helices, CoNitPhOMe and MnNitPhOMe hereafter, whose structure is shown in Figure 1a. These helices comprises Mn^{2+} and Co^{2+} centers bridged by stable nitronyl-nitroxide organic radicals, the NitPhOMe moiety.^{5, 6} In the case of the Co^{2+} helix interesting dynamic effects have been observed and associated to the Ising nature of this ion.^{7,8} The compounds crystallize in fully chiral P3₁ or P3₂ space groups. The chirality has been rapidly resolved by measuring the X-ray natural circular dichroism (XNCD) in five crystals of each compound at room temperature. An intense dichroic signal was observed for each crystal but with opposite sign for approximately half of them, in agreement with the odd-parity of the natural dichroism and the employed synthetic procedure that does not favour one particular enantiomer.

The room temperature screening has allowed the selection of two single crystal of opposite chirality for both MnNitPhOMe and CoNitPhOMe, which have then been measured at low temperature using the 15 Tesla cryomagnet of the beamline. A series of absorption spectra in function of the magnetic field and the helicity of the circular polarization have been collected in order to extract the XMCD, the XNCD and the XM χ D (Fig. 1b). Magnetic circular dichroism (XMCD) measured at 2.25 K and 1 T applied field shows again a significant signal, in this case with the same sign for both types of enantiomers, as expected for the parity-even, time reversal-odd character of XMCD.

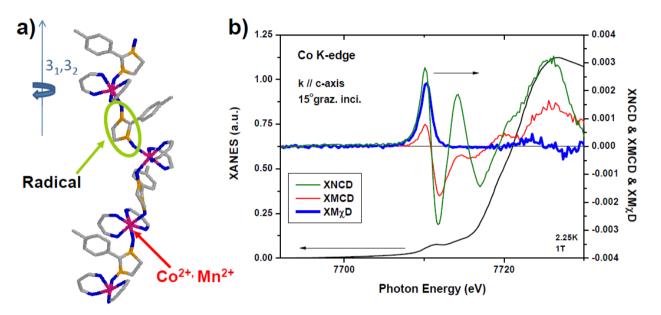


Fig. 1. Structure of the MNitPhOMe systems (M=Co and Mn) (a) and the experimental XNCD, XMCD and XM χ D spectra obtained from the characterization of a single crystal.

It is worth noticing in Figure 1b that the XM χ D spectrum differs significantly from XMCD and XNLD, thus excluding that its strong intensity results from experimental artefacts. Moreover, a preliminary data analysis suggests a much stronger XM χ D signal in the case of the Co²⁺ based system, opening the possibility to establish correlations between the chemical composition and magneto-chirality effects.

References

- 1. G. Wagnière and A. Meier, *Chem. Phys. Lett.*, 1982, **93**, 78-81.
- 2. L. D. Barron and J. Vrbancich, *Molec. Phys*, 1984, **51**, 715-730.
- 3. G. Rikken and E. Raupach, *Nature*, 1997, **390**, 493-494.
- 4. J. Goulon, A. Rogalev, F. Wilhelm, C. Goulon-Ginet, P. Carra, D. Cabaret and C. Brouder, *Phys. Rev. Lett.*, 2002, **88**, 237401.
- 5. A. Caneschi, D. Gatteschi, P. Rey and R. Sessoli, *Inorg. Chem.*, 1991, **30**, 3936.
- A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M. G. Pini and M. A. Novak, *Angew. Chem. Int. Ed.*, 2001, 40, 1760-1763.
- L. Bogani, A. Caneschi, M. Fedi, D. Gatteschi, M. Massi, M. A. Novak, M. G. Pini, A. Rettori, R. Sessoli and A. Vindigni, *Phys. Rev. Lett.*, 2004, **92**, art. no.-207204.
- 8. E. Heintze, F. El Hallak, C. Clauß, A. Rettori, M. G. Pini, F. Totti, M. Dressel and L. Bogani, *Nature Mater*, 2012, advanced on-line publication, doi:10.1038/nmat3498.