ESRF	**Experiment title:** Designer Magnetochiral Dichroism: Eu(II) as the optimal solution for strong magnetoelectric coupling in lanthanoid coordination complexes	**Experiment number:** CH-6242
Beamline: ID12	**Date of experiment:** from: 21.06.2022 to: 27.06.2022	**Date of report:** 12.09.2022
Shifts: 18	**Local contact(s):** Andrei Rogalev	*Received at ESRF:*

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Report:

Introduction

The ability to individually adress molecular centres on a surface is a requirement for future device implimentation of molecular systems.[1] One way to achieve such control is through coupling between local electric fields and the magnetic moment of single molecules. Such a coupling is possible in molecules which display the magnetoelectric effect, where the absence of inversion symmtry leads to efficient coupling of the magnetic moment of individual molecules and the local magnetic field.[2] One way to check that there is an efficient coupling between small local electric fields and the magnetic moment of the molecule is through the observation of MagnetoChiral Dichroism (MChiD). We have previously measured (CH-5357) X-ray MagnetoChiral Dichroism (XMChiD) on $Na_5[Ho(ODA)_3](BF_4)_2 \cdot 6(H_2O)$, where ODA^{2-} = oxydiacetate, Figure 1.[3] The XMChiD signal was observable at the L_3-edge of Ho, but it was weaker than anticipated for a 4f system. This is possibly due to the very localised 4f electrons which are little affected by the chirality of the surrounding ligand scaffold, thus giving rise to a small XMChiD signal. In order to obtain a larger XMChiD signal we sought to increase the hybridisation between the 4f and 5d orbitals, since the 5d orbitals have a larger radial extension than the 4f orbitals and are thereby more affected by the chiral ligand environment. In Eu(II) the admixture between the 5d and 4f orbitals should be larger than for any Ln(III) ion. Therefore, we sought to measure XMChiD on single crystals of the resolved Eu(II) complex $EuI_2(^iPrNH_2)_4$ ($^iPrNH_2$ = isopropylamine). Due to the inherent air- and moisture sensitivity of the titled Eu(II) complexes, measurements of the XMChiD of these complexes was not possible. Instead it was decided to measure on $Na_5[Dy(ODA)_3](BF_4)_2 \cdot 6(H_2O)$ and $Na_5[Gd(ODA)_3](BF_4)_2 \cdot 6(H_2O)$ in order to get further information about the XMChiD of molecular lanthanide systems. Here Gd(III) is interesting as it has a ground multiplet without orbital angular momentum.

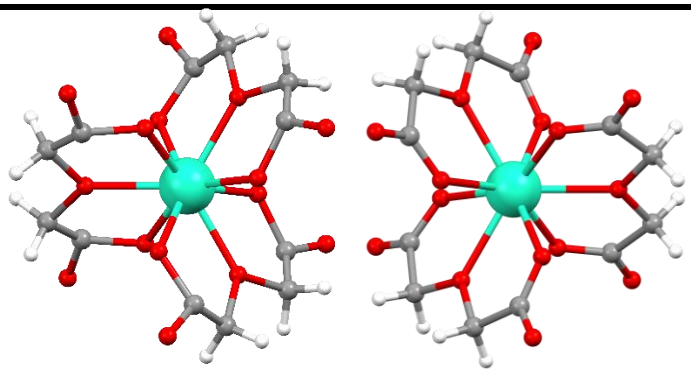

Figure 1. The two chiralities of [Dy(ODA)3]3- viewed along the crystallographic C_3 axis. Color code: O, red; C, gray; H, white and Dy, cyan.

Results

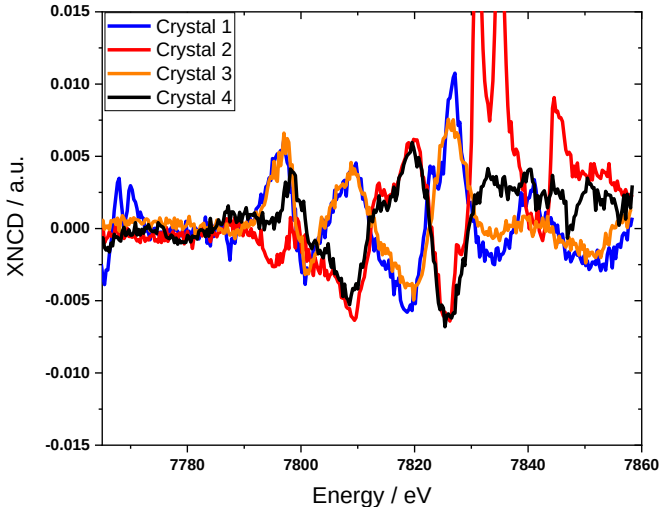

Figure 2. XNCD at the Dy L_3-edge of 4 single crystals of **1** measured in zero magnetic field and at 295 K. Crystals 1 and 3 are the Δ helicity while crystals 2 and 4 are the Λ helicity.

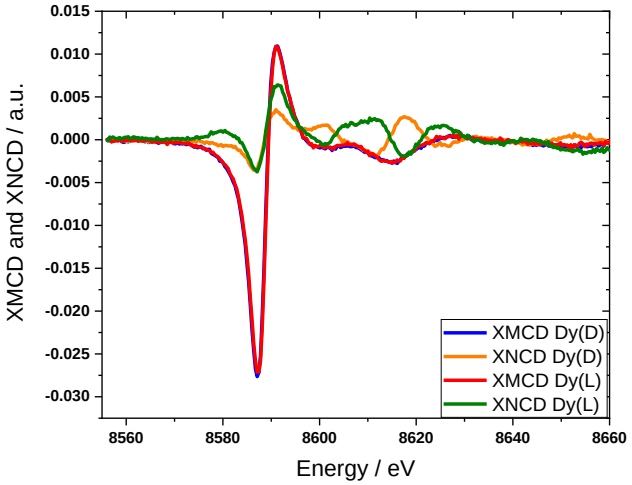

Figure 3. XNCD and XMCD at the Dy L_2-edge of single crystals with either a Δ or Λ helicity of **1** measured at 2 T and at 2.7 K.

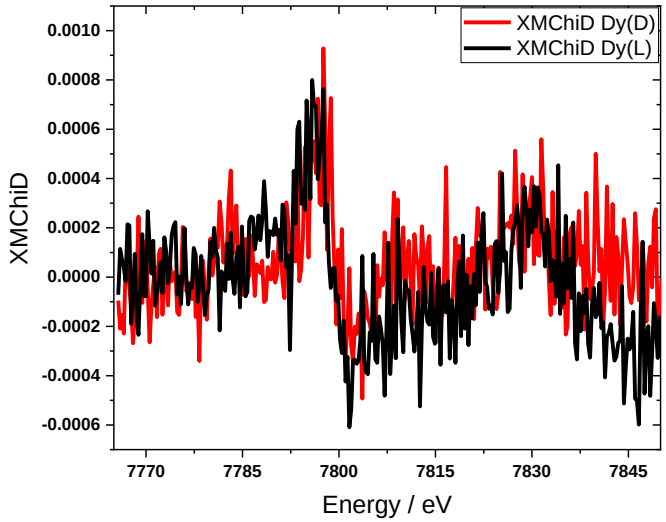

Figure 3. XMChiD spectra at the Dy L_3-edge of single crystals with either a Δ or Λ helicity of **1** measured at 2 T and at 2.7 K.

$Na_5[Ln(ODA)_3](BF_4)_2 \cdot 6(H_2O)$ crystallises in the trigonal spacegroup *R*32 as large (3mm x 3mm x 1mm) hexagons. Upon crystallisation the complexes resolve in a Δ or Λ configuration, Figure 1. Using single-crystal X-ray diffraction the chirality of each crystal was checked at The Department of Chemistry, University of Copenhagen prior to the beamtime. For the measurements of XMChiD it is important to have crystals with similar amplitudes of the X-ray Natural Circular Dichroism (XNCD), therefore, the XNCD in zero magnetic field was measured for 4 crystals (two of each chirality Δ or Λ) for both the Dy and Gd complexes, Figure 2. In the following the results obtained on $Na_5[Dy(ODA)_3](BF_4)_2 \cdot 6(H_2O)$ (**1**) will be discussed as the Gd data are still being evaluated. All the measurements on **1** were performed at 2.7 K if not stated otherwise.

All four crystals of **1** showed an XNCD of similar magnitude, Figure 2. For the subsequent measurements of the X-ray Magneto Circular Dichroism (XMCD) and XMChiD at the L_2- and L_3-edges of Dy, crystals 3 and 4 were chosen as their XNCD intensities were comparable, and crystal 4 did not show the same artifacts at 7835 eV as crystal 2. It should be mentioned that during the beamtime much time was used to orient the crystals properly such that diffraction peaks in the XANES were avoided. Additionally, we also observed radiation damage in the beginning of the beamtime, but by minimizing the intensity of the X-ray beam to a minimum the radiation damage was avoided. In our previous measurements on $Na_5[Ho(ODA)_3](BF_4)_2 \cdot 6(H_2O)$ the same degree of radiation damage was not observed. We attribute this to the fact that the beamline at ID 12 was upgraded since our previous visit.

XMCD and XNCD at 2 T were measured at both the L_2- and L_3-edges of Dy, see Figure 3 for the measurements at the L_2-edge. The XNCD spectra of crystals of opposite chirality should be mirror images of each other. This is the case in the present measurements above 8595 eV, but not below. We believe that this is due to artifacts in the crystals.

The observed XMChiD spectra of **1** at both the L_2- and L_3-edges were much more noisy than for the analogous Ho system. Unfortunately, we did not see a clear sign of XMChiD in **1**, neither at the L_2- nor L_3-edge. This is for instance seen in Figure 4, where we do not observe a clear mirroring of the XMChiD signal of the Δ and Λ complexes of **1**.

In addition to measurements at 2 T for **1**-Δ and **1**-Λ measurements were also performed at 7 T for **1**-Λ at the Dy L_3-edge. This was done since **1** at 2 K switches its anisotropy from easy axis to easy plane at 3 T. These measurements were performed to see how the XMCD and XMChiD changes when the anisotropy axis of the complex changes. No significant change was observed.

1. Vincent, R.; Klyatskaya, S.; Ruben, M.; Wernsdorfer, W.; Balestro, F., Electronic read-out of a single nuclear spin using a molecular spin transistor. *Nature* **2012,** *488* (7411), 357-60.
2. Eerenstein, W.; Mathur, N. D.; Scott, J. F., Multiferroic and magnetoelectric materials. *Nature* **2006,** *442* (7104), 759-65.
3. Mitcov, D.; Platunov, M.; Buch, C. D.; Reinholdt, A.; Dossing, A. R.; Wilhelm, F.; Rogalev, A.; Piligkos, S., Hard X-ray magnetochiral dichroism in a paramagnetic molecular 4f complex. *Chem Sci* **2020,** *11* (31), 8306-8311.