	Experiment title: **Hidden ferrimagnetism and the Dzyaloshinskii-Moriya interaction in $Fe_2Mo_3O_8$ studied by X-ray resonant scattering**	Experiment number: **HC-3568**
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Report

Scientific Background

In this experiment we expected to obtain unique information about the absolute configurations of spins in a unit fell of the $Fe_2Mo_3O_8$ aiming to determine the sign of the Dzyaloshinskii ï Moriya interaction in this substance. Our plan was to measure the forbidden Bragg 0003 reflection (d_B=15°) at the Fe K-edge (7112 eV) both in para- ferro- and antiferromagnetic phases below T_N=60K applying a magnetic field $\varepsilon_0 H \sim 0.2$ T along the c-axis. To our great regret, we were not able to obtain a satisfactory results because the sample was damaged during handling. Therefore we changed a sample to $SmFe_3(BO_3)_4$ single crystal. This compound was previously well characterized by magnetic and spectroscopic techniques [1-3] and a giant magnetodielectric effect in an external magnetic field was observed. Its space group *R*32 is comparable with enantiomorphism; that is to say, there should exist two chiral atomic arrangements, left- and right-handed. Recently, chiral crystallization of functional materials attracts much attention, since simultaneous violation of time and space inversion symmetry evokes unusual electromagnetic phenomena such as multiferroics [4] or skyrmion crystal [5]. An enantiopure crystal may be the ideal form of a functional material having chirality-related properties, but the existence of domains and defects strongly influences their macroscopic responses and chirality-related activities are compensated between enantiomers. Nobody can predict the distribution of right- and left-handed domains during crystalization. Currently, a few experimental approaches are known to make a direct visualization of chiral domains, one is given by resonant X-ray diffraction with circularly polarized beams [6]. XNCD is a unique method well developed at the ID12 beamline, which distinguishes right- and left- handed structures, but it gives information averaged over the beam size. To study chiral domains distribution we need to use a size of a beam less that the domain size and usage of X-ray lenses gives us such possibility. An interesting structural feature of $SmFe_3(BO_3)_4$ is a presence of chiral chains formed by edge-shared FeO_6 octahedra, which are propagated along the trigonal *c*-axis. To demonstrate the XNCD images technique practically, we imaged a chirality-domain distribution in a magnetoelectric $SmFe_3(BO_3)_4$ crystal.

Experimental details

In the experimental implementation of XNCD mapping concept, circularly polarized X-rays from a helical undulator insertion device were monochromatized to photon energy near the Fe *K*-edge in the *c*-axis direction of the single crystal. The beryllium X-ray refractive lenses[36] focused the circularly polarized X-rays down to 20×200 μm^2 at the sample position . The irradiation area on a sample surface was scanned by shifting the translation position of the whole sample holder. To obtain chirality-domain

images, the sample was scanned perpendicular to the beam. At each position, the XNCD intensity was measured with circularly polarized beams.

Results

The XNCD spectra were obtained as the direct difference of two X-ray absorption spectra recorded with right- and left-circularly polarized X-rays. For the sake of simplicity, the trigonal *c*-axis was set collinear in the direction of the exciting X-ray beam in order to get rid of undesirable X-ray birefringence and X-ray linear dichroism effects. The sample was moved stepwise in both the *x* and *y* directions. We focused on studying the XNCD signal in the pre-edge of Fe K-edge spectrum and observed the inversion of its sign during scanning over the crystal surface. All spectra exhibit XNCD; that is, the intensities of pre-edge peaks are anticorrelated, when beam with circular polarization is moving on the surface of the crystal from one enantiomorphous domain to another, the peaks are maximum and minimum, respectively. So, we observed a distribution of the left- and right-handed domains. In the border regions, the signal magnitude changed, which is reflected in Fig. 2 as color change.

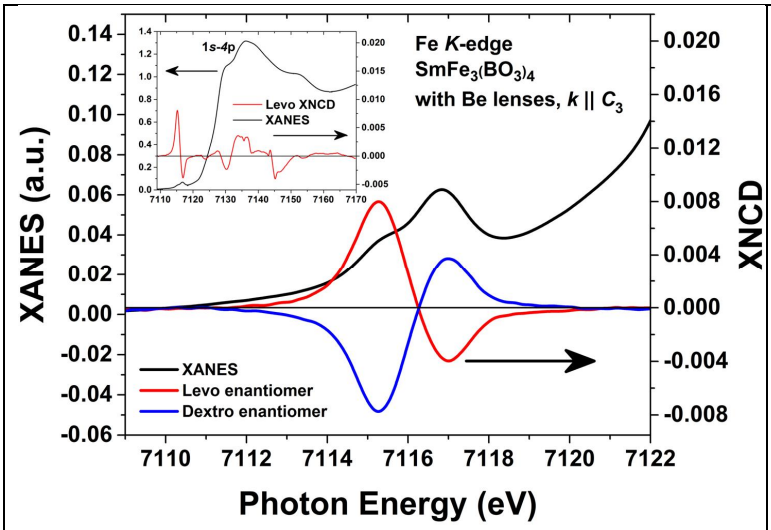

Figure 1. Experimental dichroism signals obtained from XANES experiments at the Fe *K*-edge from two enantiomorphous positions of the racemic $SmFe_3(BO_3)_4$ single crystal recorded with the X-ray wavevector parallel to the trigonal *c*-axis: pre-edge XANES structures from 7112 eV to 7119 eV can be assigned to a set of 1*s*-3*d* transitions; near-edge structures to 1*s*-4*p* shape resonances. On the inset: the black curve is the corresponding averaged XANES spectrum, and the red curve is the corresponding XNCD spectrum for one enantiomer extending to whole measured range.

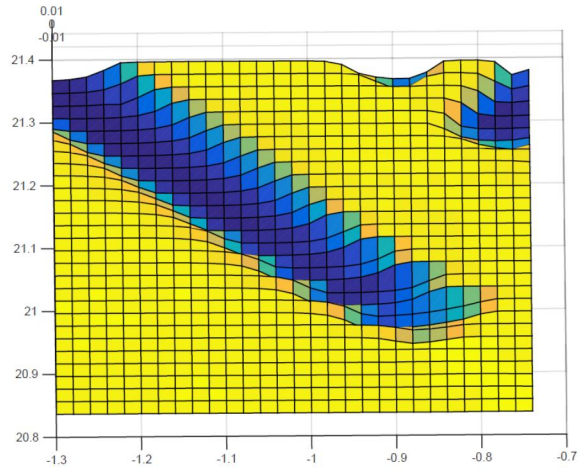

Figure 2. Mapping of twins in the racemic $SmFe_3(BO_3)_4$ single crystal along the trigonal *c*-axis extracted from XNCD signals measured at the Fe *K*-edge as a function of coordinates. Image size: 560×560 μm^2.

Report Summary

In conclusion, we have demonstrated and exploited X-ray Natural Circular Dichroism for visualizing the spatial distribution of enantiopure domains in complex magnetoelectric $SmFe_3(BO_3)_4$ single crystal. The XNCD spectra as an element selective probe of local chirality and the new approach to non-destructive twins mapping establish the feasibility of mapping and understanding the orientations of enantiomers and their structural arrangement. These results change and improve significantly our understanding of the crystallographic orientation of the racemic single crystal. Although the experiment looks trivial, it proved to be delicate because fairly high beam stability is required over long periods of times since inverting the domains is very time-consuming.

References

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