ESRF	**Experiment title:** Observation of microscopic magnetoelectric effects in field induced $GdFe_3(BO_3)_4$	**Experiment number:** HC-3570
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Report:

The aim of this proposal was to investigate the magnetism induced by the electric field on magnetoelectric (ME) $GdFe_3(BO_3)_4$ single crystal using X-ray magnetic circular dichroism. But we could not measure any noticeable element-specific magnetic response to the electric field. Apparently, one of the principal difficulties that we had during measurements was the twinning in the crystals. This crystal twinning is very rarely discussed in the literature, but it can greatly affect the detectable ME effect, in particular, if crystals are composed of twin domains with opposing polarities. Unfortunately, it is almost impossible to identify the twinning using traditional XRD analysis (especially, the domain distribution in a whole crystal).

To investigate the element-specific magnetic response induced by the electric field we had to have information from enantiomeric crystals. During the experiment, we had tried to measure the X-ray natural circular dichroism (XNCD) effect in different ferroborate single crystals in order to get an understanding of twinning. Because XNCD obtained with left- and right-handed circularly polarized incident X-rays is a structural effect, therefore the handedness of the screw crystal axis could be examined by comparing an XNCD sign on the different samples or sample areas

All X-ray spectra were recorded using a total fluorescence yield detection mode in “backscattering” geometry using Si photodiodes at the room temperature. XANES spectra showed in Figure 1 were obtained as the simple arithmetic average of the collected spectra. The difference of these spectra is related to a slightly different electronic structure and some influence of self-absorption effect (the measurements were provided at the different synchrotron beam conditions, as well as using different detectors). But it will not influence the XNCD and we will not discuss it below. XNCD spectra were obtained as the direct difference of two X-ray absorption spectra recorded with right- and left-circularly polarized X-rays. A fairly intense XNCD signal was detected at the Fe K-edge for different samples which were measure for the comparison (Figure 1). The XNCD signal itself at the Fe K-edge could be assigned to the electric dipole-electric quadrupole interference term (E1: E2) which contributes to the rank-2 pseudo deviator part of the optical activity tensor. Our interpretation and the large magnitude of the effect measured at the Fe K-edge were confirmed by theoretical calculations more than once by the ID12 beamline group.

In Figure 1 we see, that all spectra exhibit XNCD (it is seen between 7110 and 7120 eV); the intensities of pre-edge peaks are anticorrelated, from one racemic sample to another. The XNCD signal intensity at the pre-edge is related to a difference in electronic structure as seen by left and right circularly polarized photons due to the structural chirality and the magnitude of these strongly depend upon the presence of enantiomers (number of twins under the X-ray beam spot). Unfortunately, the size of the X-ray beam was larger than the size of the twins and we were not able to perform an experiment to determine the twin sizes. The fact that the $GdFe_3(BO_3)_4$ and $Ho_{0.5}Nd_{0.5}Fe_3(BO_3)_4$ crystals were racemic is further confirmed by suppressed XNCD signal at the Fe K-edge. Note that the XNCD signal at the Fe K-edge in an enantiopure $NdFe_3(BO_3)_4$ is about 1% with respect to the edge jump. In the case of $GdFe_3(BO_3)_4$ crystal, we see a smaller and opposite signal, due to the fact that there is a predominance of enantiomers with another chirality. As for

$SmFe_{2.95}Al_{0.05}(BO_3)_4$, it is given for comparison to show a larger opposite signal compared to the $GdFe_3(BO_3)_4$ crystal.

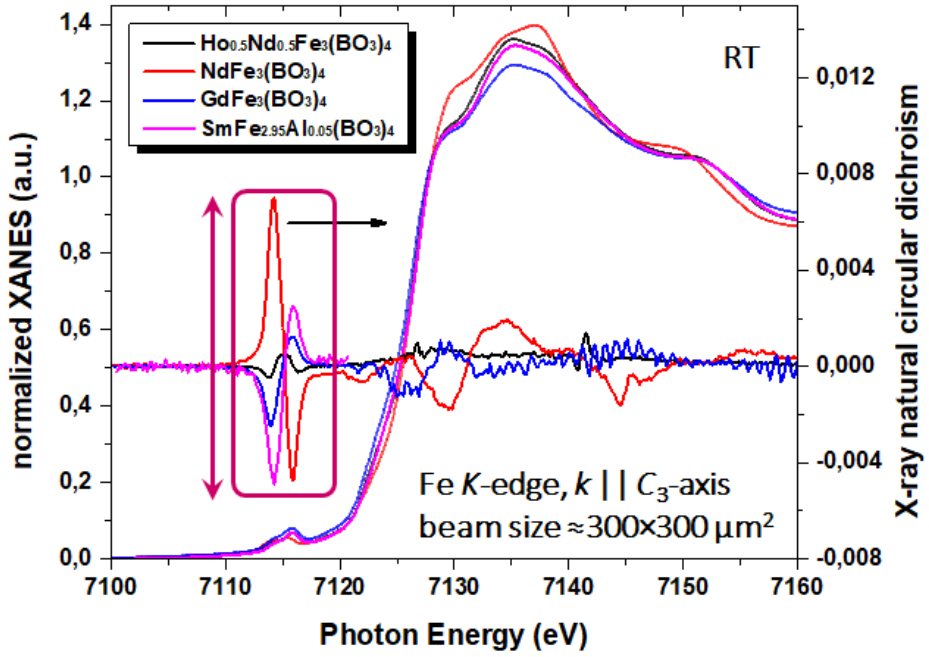

Figure 1. Normalized XANES and XNCD spectra in different iron borates across the Fe K edge of recorded at room temperature.

Unfortunately, our results showed that all the $GdFe_3(BO_3)_4$ single crystals were twinned. Therefore, during the experiments, we have not seen the influence of the electric field on magnetism. Apparently, an existence of inversion twins in our crystal strongly affects the element-specific magnetic response to the electric field. Data obtained will be taken into account to grow new high-quality single crystals and the subsequent selection of high-quality (twin-free) crystal specimens will be performed. We plan to submit several new ESRF proposals to be able to identify the new crystals by the XNCD technique.

One of the principal difficulties that we had during measurements was the limitations of the mechanical precision for the translation motors. Besides, it was not possible to focus the beam down to a 2 mkm x 2 mkm spot size in order to be able to measure the lowest domains as possible. This yielded to the impossibility of collecting XNCD data from different sample points and make twinning maps during the experiment. As a next step, we hope that combining the advantages of a new EBS-ESRF beam (radiation coherence, beam stability, and micro focusing) and ID12 beamline upgrade with precision mechanics based on stepping piezo motors, we will be able to make a mapping of the crystals, the understanding of growth parameters-structure-properties relationships in $GdFe(BO_3)_4$ crystals and not only, as well as perform the investigation of element-selective magnetism induced by the electric field on $GdFe_3(BO_3)_4$ single crystals definitely. The results are very encouraging and we hope to carry out the full experimental program of the experiment later.

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