ESRF	**Experiment title:** Probing the charge ordering phenomenon in electronic multiferroics using resonant x-ray diffraction	**Experiment number**: HC-3736
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Shifts: 18	**Local contact(s)**: Stéphane Grenier	*Received at ESRF:*

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Report:

During this beamtime, we performed resonant X-ray diffraction (RXD) measurements at the Fe *K*-edge and Co *K*-edge on the Fe and Co-based ludwigites. The purpose of the experiment was to track charge order signatures using RXD in both compounds and to reveal its coupling with the magnetic ordering at low temperature. This experiment was challenging due, principally, to the sample sizes (~100µm*50µm*50µm for Fe_3BO_5 and ~ 200µm*80µm*80µm for Co_3BO_5). Despite this difficulty, the experiment was feasible and satisfactory since we managed to orient and measure both samples.

For this study, we used the Kappa diffractometer and a closed cycle He cryostat in azimuthal geometry. The Fe_3BO_5 and Co_3BO_5 samples were glued at the tips of 100 µm diameter quartz capillaries. Then, the capillaries were mounted on a Copper sample holder which was inserted inside the cryostat. To save time, both Fe_3BO_5 and Co_3BO_5 samples were mounted together on the Copper sample holder and we took advantage of the precise translational stage of the Kappa diffractometer to go from one sample to another. Two different edges [Fe *K*-edge (7.12 keV) and Co *K*-edge (7.72 keV)] were used with a 100 µm-size focused beam which allowed to measure resonant effects in both Fe_3BO_5 and Co_3BO_5 samples. By using the closed cycle He cryostat, we were able to realize precise temperature dependence measurements, from 32 K to 325 K.

Figure 1 **(a)** shows a Lscan along the (0 2 L) direction in the Fe_3BO_5 sample at both 32 K and 325 K (*i.e.* below and above the charge ordering transition temperature, T_{CO} ~ 283 K). At 32 K, below T_{CO}, superstructure peaks are observed at L = *n*/2 (*n* an integer). These additional low temperature peaks are the signature of a structural distortion, concomitant with the charge ordering. This structural distortion corresponds to a doubling of the cell along the ***c***-axis. This observation confirmed a previous work, where the structural distortion was already mentioned [1].

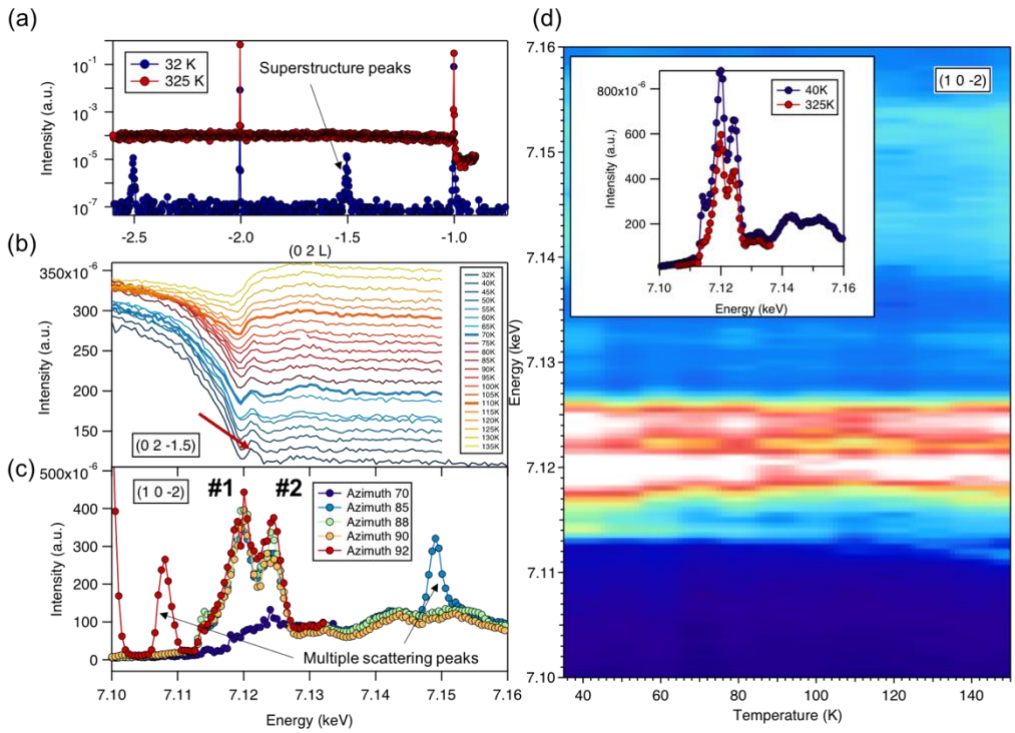

Figure 1: **(a)** Lscans along the (0 2 L) direction at 32 K and 325 K in the Fe_3BO_5 sample. The scattering intensity is plotted with logarithmic scale. The data are shifted vertically for clarity. **(b)** Energy scans of the (0 2 -1.5) reflection at different temperatures in the Fe_3BO_5 sample. The data are shifted vertically for clarity. **(c)** Energy scans of the (1 0 -2) reflection at different azimuthal angles. **(d)** Energy scan intensity map of the (1 0 -2) reflection as function of the temperature. Inset: energy scans of the (1 0 -2) reflection at 40 K and 325 K.

Figure 1 **(b)** reports energy scans of the (0 2 -1.5) reflection in the Fe_3BO_5 sample, near the Fe *K*-edge, at several temperatures, from 32 K to 135 K. A small resonant effect is observed around 7.120 keV and in the low temperature data (see red arrow). Nevertheless, an absorption correction is required to reveal its complete resonant profile. Figure 1 **(c)** and **(d)** show an azimuthal and temperature dependence of the energy scans on the (1 0 -2) reflection in the Fe_3BO_5 sample. In Figure **(c)**, a resonant profile is observed with the presence of two peaks at 7.120 and 7.125 keV (peaks **#1** and **#2**). In contrast to the 7.108 or 7.150 keV peaks, these **#1** and **#2** peaks are energy independent when changing the azimuthal angle Ψ, meaning that they cannot be attribute to multiple scattering peaks. In addition, the intensity of the (1 0 -2) reflection is zero just below the Fe *K*-edge indicating that this reflection is purely resonant. The temperature dependence of this resonant reflection is shown on Figure 1 **(d)**. No clear effects are observed, neither at both magnetic ordering transitions (T_{N1} ~ 70K and T_{N2} ~ 110K), nor above the charge ordering transition temperature [see inset of the Figure 1 **(d)**]. This observation indicates that the (1 0 -2) reflection is not a signature of the crystallographic site where the charge ordering occurs. Then, we measured energy scans on many other reflections which are not presented here. These energy scans were only recorded at low temperature due to a lack of time. Finally, despite our preparation of the Co_3BO_5 sample, we did not have enough time to start the low temperature measurements on this sample, especially because of a technical issue, which led to one night of measurement lost.

To short, this experiment was challenging, but feasible and satisfactory. Despite the small sizes of the samples, we were able to measure many reflections at different temperatures, energies, azimuthal angles and at two different edges. The data analysis is still in progress: we are working on a procedure to correct the absorption and we are also simulating the resonant profile of the measured reflections using the FDMNES software [2], in order to compare our data with the charge order model proposed in [1]. Yet, more beamtime is needed to conduct a complete temperature dependence study on the other reflections we have measured at low temperature during this experiment. In addition, it would be interesting, for a comparison, to prospect the other ludwigite sample (Co_3BO_5), where a charge ordering was suspected but not directly detected [3]. This was not possible this time because of limited time allocation. Therefore, we will propose to continue this study in the next cycle.

Reference:

[1] P. Bordet and E. Suard, *Phys. Rev. B* **79**, 144408 (2009).
[2] Y. Joly, *Phys. Rev. B* **63**, 125120 (2001).
[3] D. C. Freitas et al., *Phys. Rev. B* **94**, 174409 (2016).