ESRF	**Experiment title:** SINGLE-CRYSTAL X-RAY DIFFRACTION STUDY OF THE LOW TEMPERATURE STRUCTURE OF NICKEL FERRITE	**Experiment number**: HC-5287
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Names and affiliations of applicants (* indicates experimentalists):

*Stéphane Grenier, Institut Néel, CNRS, Grenoble, France

*Laura Chaix, Institut Néel, CNRS, Grenoble, France

*Claire Colin, Institut Néel, CNRS, Grenoble, France

*Tristan Viallet, Institut Néel, CNRS, Grenoble, France

Yves Joly, Institut Néel, CNRS, Grenoble, France

Scientific context and aim:

The Nickel Ferrite $NiFe_2O_4$ (NFO) is known to cristallize in the cubic Fd-3m space group and belongs to the inverse spinel family where the tetrahedral A-site are supposed to be fully occupied by Fe3+ only and the octahedral B-site are occupied by both Ni2+ and Fe3+. It ferrimagnetically orders under 870K. Numerous compounds of this family shows a wide variety of interesting properties, multiferroicity amongst them. NFO has been reported to display a structural transition at 98K concomitant to the appearance of an electrical polarization which would make it a multiferroic at low temperature [1]. The occurance of this ferroelectricity was explained as originating from a cationic order between the Fe^{3+} and the Ni^{2+} on the octahedral B-site. To further explore this possible cationic order, we performed resonant X-ray diffraction (RXD) measurements at the Fe *K*-edge and Ni *K*-edge on our NiFe2O4 single-crystals. The purpose of the experiment was to (i) characterize the inversion ratio of our samples (*i.e.* the fraction of Ni2+ occupying the octahedral and/or tetrahedral sites) (ii) and to confirm an eventual structural transition between high and low temperatures as well as a cationic order on the octahedral B-site.

Technical details and results:

For this study, we used the Kappa diffractometer and a closed cycle He cryostat in azimuthal geometry. The NiFe2O4 sample was glued with silver paint on a copper plate. The sample was a NFO slide with a <110> normal direction. Then, it was mounted on the sample holder which was inserted inside the cryostat. Two different edges [Fe *K*-edge (7.112 keV) and Ni *K*-edge (8.332 keV)] were used. The cryostat was there to reach low temperatures so that we could probe the transition expected around 98K. We performed energy scans of several Bragg peaks at 22K and 300K with a fixed azimuth. We also measured forbidden reflections and their azimuthal dependency. Each peak can be categorized through their form factor, indicating whether they are representative of a specific site in the compound. Therefore, some Bragg reflections will be representative of only the tetrahedral A-site whereas others will be representative of the octahedral B-site. The simulations were calculated with FDMNES software and the absorption correction was firstly done through the following simple cross product:

$$I_{corrected\ peak} = I_{peak} \times \frac{I_{corrected\ simulated\ reference}}{I_{reference}} \qquad [A]$$

It is important to note the quality of this correction depends on the quality of the measurement of the chosen reference peak and on the validity of the simulated model.

Figure 1 (a) displays the corrected energy scans, close to the Fe and Ni K-edges, of the (6 2 0) Bragg peak, which is representative of the tetrahedral A-site. The blue curves were collected at 22 K, the orange ones at 300K. We can observe that the amplitude of the signal at the Fe K-edge is way higher than the almost flat curve at the Ni K-edge. This is similar to the FDMNES simulations [see Figure 1 (b)] using a model considering Fd-3m symmetry and only Fe on the tetrahedral A-site. In addition looking at the temperature dependence, one can observe that there is no obvious difference between both 22 K and 300 K.
From these measurements and the simulation, we can conclude that there is almost no Ni on the tetrahedral A-site compared to the amount of Fe, which would confirm that the inversion parameter of our sample is close to 1. Note that the inversion parameter x is defined as $[Fe_xNi_{1-x}]_{Td}\,[Fe_{2-x}Ni_x]_{Od}\,O_4$. The inversion parameter $x = 1$ is expected in a full inverse spinel structure, *i.e.* Ni^{2+} occupying only the octahedral B site. Quantitative analysis are in progress to estimate the real inversion parameter value.

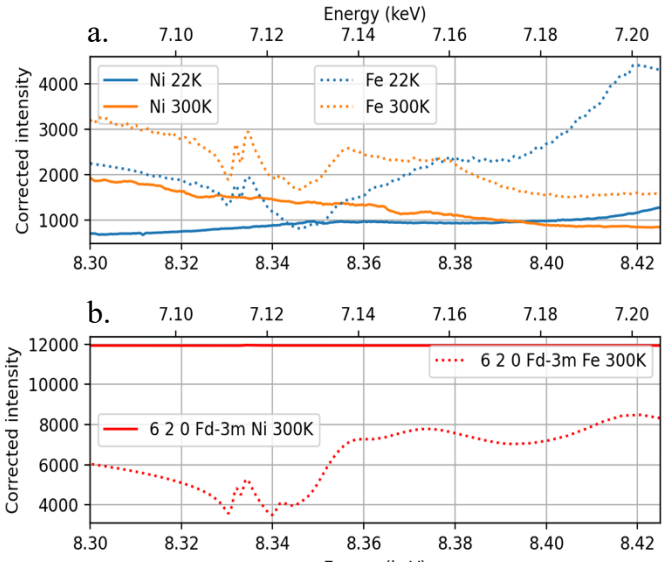

Fig 1: (a) Energy scans of the Fd-3m <6 2 0> tetrahedral peak. The plain curves are at the Ni K-Edge and the dotted curves are at the Fe K-Edge. (b) FDMNES simulations of the <6 2 0> in the Fd-3m structure.

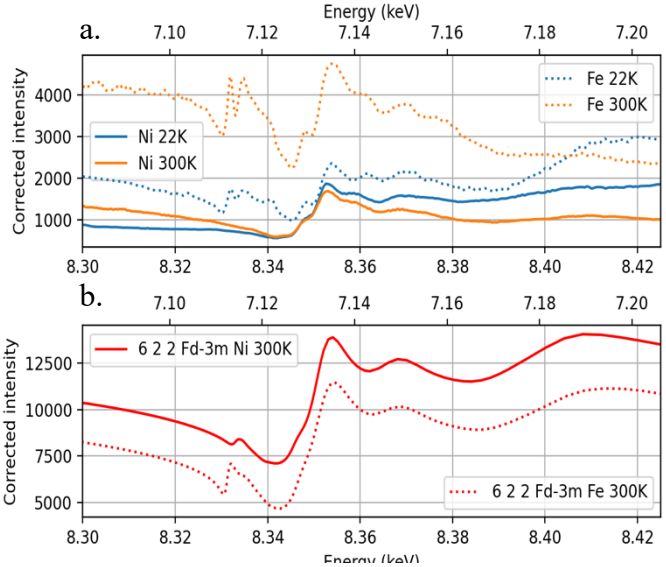

Fig 2 : (a) Energy scans of the Fd-3m <6 2 2> octahedral peak. The plain curves are at the Ni K-Edge, the dotted curves are at the Fe K-Edge. (b) FDMNED simulations of the <6 2 2> in the Fd-3m structure.

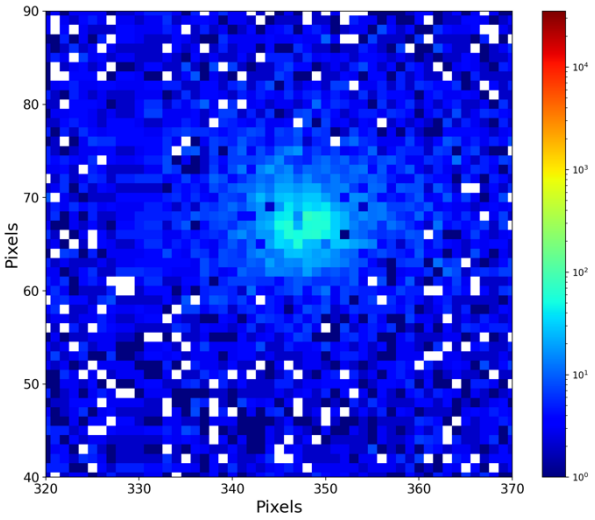

Fig 3 (a): 2 4 0 peak image of the detector at 7.08998 keV below the pre-peak and the main Fe K-Edge.

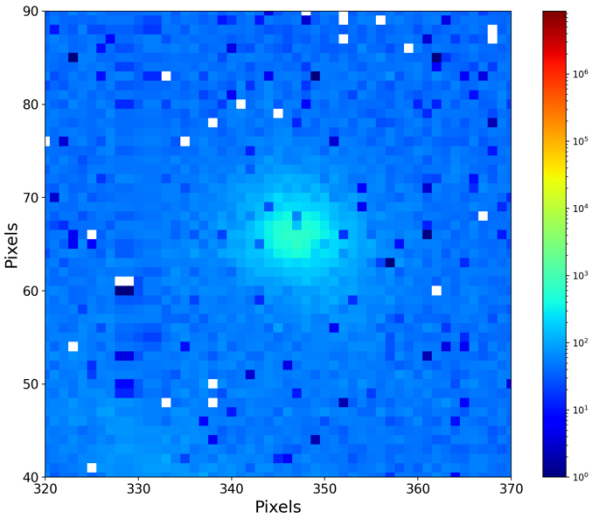

Fig 3 (b): 2 4 0 peak image of the detector at 7.1186 keV above the main Fe K-Edge.

Figure 1 (b) displays the corrected energy scans, close to the Fe and Ni K-edges, of the 6 2 2 peak, which is representative of the octahedral B-site. As expected, the amplitude of the signal at the Ni K-edge is similar to the one at the Fe K-edge 22K, as also observed in the FDMNES simulation shown on Figure 2 (b). Note that the FDMNES simulations have been done for an equal amount of Fe^{3+} and Ni^{2+} on the octahedral B-site. This suggests that the octahedral B-site seems to be similarly populated by Fe and Ni, confirming the above conclusion, i.e. an inversion parameter close to 1. However, there is an anomaly for the signal at the Fe K-edge 300K exhibiting a larger amplitude than the other energy scans. In addition, there is also no clear difference between the low and room temperature, the features displayed are sensitively similar, except the larger amplitude at the Fe K-edge at 300K which needs to be clarified.
From these measurements and the simulations, we can conclude that the B-site seems to be similarly populated by Iron and Nickel, however further FDMNES simulations are necessary to draw quantitative conclusions from these data.
From these measurements we can't conclude that there is a structural distortion of the sample space group at low temperature, which leads to wonder whether there is a real apparition of ferroelectricity linked to this structural transition. Further experiments will be needed to confirm this result.

The last main result of this study concern the observation of forbidden peaks at 300 K. Indeed as shown on Figure 3 displaying the image of the detector, forbidden peak of type $0kl,\ k+l \neq 4n$ and $h00,\ h \neq 4n$ (forbidden for the Fd-3m space group) can be detected both before the edge [Figure 3(a)] and after the resonance [Figure 3(b)]. This means that this peak is not purely resonant and therefore indicate that the structure has a lower symmetry than expected.

The existence of forbidden peaks (2 8 0 and 2 4 0) led to a new hypothesis on the structure through the analysis of the extinction rules of Fd-3m subgroups: The right structure to be confirmed would be F-43m. Further diffraction experiments are planned in order to confirm this result.

Summary:
To short, we were able to make energy scans with fixed azimuth for many reflections at 20 and 300 Kelvins, at two different edges. **No clear temperature dependence could be observed through this experiment**. It allowed us to harvest the necessary data to **calculate the inversion ratio**, study the existence of a **cationic order on the octahedral site** and study some **purely resonant reflections**. This is a preliminary analysis because it is necessary to compare these results with another method for the absorption correction. In addition, we also performed, during our beamtime, an **azimuthal dependence of the forbidden peaks. The analysis of these data is still in progress.** Moreover, since forbidden reflections were measured, we need to carry more FDMNES simulations with the correct crystallographic structure. Further diffraction experiment are also required to **determine the right structure**.

Reference:
[1] "Ferroelectric order associated with ordered occupancy at the octahedral site of the inverse spinel structure of multiferroic NiFe2O4", Dey, J. K., Chatterjee, A. et al., Physical Review B, 2019.