EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: XAS and XMCD studies of the low temperature magnetic and electronic properties of the Nickel Ferrite.	**Experiment number**: HC-5207
Beamline: ID12	**Date of experiment**: from: 25/04/2023 to: 01/05/2023	**Date of report**: 21/08/2023
Shifts: 18	**Local contact(s)**: Fabrice Wilhelm	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Laura Chaix*, Laboratory CNRS/UGA UPR2940 Institut Néel 25 rue des Martyrs BP 166 FR - 38042 GRENOBLE Cedex 9

Tristan Viallet*, Laboratory Institut Neel - CNRS UPR 2940 PLUM 25 rue des Martyrs BP 166 FR - 38042 GRENOBLE Cedex 9

Claire Colin*, Laboratory CNRS/UGA UPR2940 Institut Néel 25 rue des Martyrs BP 166 FR - 38042 GRENOBLE Cedex 9

Yves Joly*, Laboratory CNRS Institut Neel BP166 FR - 38042 GRENOBLE

Scientific context and aim:

The Nickel Ferrite $NiFe_2O_4$ (NFO) belongs to the spinel family and is receiving attention lately due to its similarity with the Magnetite (Fe_3O_4) and to the large variety of interesting properties that have been discovered in other similar spinel systems. NFO has been reported to display multiferroic properties: it exhibits ferromagnetism below 870 K and, under 98K, an electric polarization concomitant to a structural transition has been measured [1]. The existence of this transition was not confirmed by our recent Resonant X-ray diffraction experiment on single-crystals on the BM02 beamline, where no noticeable temperature dependent feature was observed. This XAS and XMCD experiment was conducted to probe through another method any sign of a structural change occurring at low temperature and to study how the magnetism is affected by this expected structural transition. Different crystallographic directions were also probed to detect any anisotropic behavior.

Technical details and results:

NiFe2O4 single crystals were prepared, oriented and cut in a form of plaquettes beforehand in order to have the <111>, <110> and <100> crystallographic directions normal to the plaquette big faces. These 3 oriented plaquettes were mounted together on the ID12 sample holder and we took advantage of the vertical translation stage to access any of the desired sample. They were placed inside the beam and the measurements were performed in reflection geometry. XMCD spectra were acquired with a magnetic field of 1T to saturate the magnetization along the incident beam ($\mathbf{k_{in}}$) and at both the Fe and Ni K-edges. We first acquired spectra on the <111> plaquette ($\mathbf{k_{in}}$ along <111>) at both 300K and 20K. Then we measured the other plaquettes ($\mathbf{k_{in}}$ along <110> and $\mathbf{k_{in}}$ along <100>) at room temperature.

Figure 1 displays the temperature dependent XAS and XMCD measurements performed on the <111> plaquette. As shown in panels (a) and (b), presenting respectively the temperature evolution of the XAS and XMCD spectra

measured at the Fe K-edges, there is no clear difference in intensity nor shape of the XAS. The XMCD signal displays a very slight difference of intensity at the pre-peak which is stronger at lower temperatures. That could be explained by the increase of the saturated magnetic moment at low temperature. The fact that the intensity of the XMCD signal at the resonance is higher for 300K is probably due to the influence of the diffraction peak (circled in red on figure 1(a)). In order to get rid of these diffraction peaks throughout the experiment we had to slightly tilt the sample holder, measure two angles very close to the desired direction and concatenate the proper parts of the measurements.

Panels (c) and (d) present the same measurements at the Ni K-edge. There is a slight difference of intensity on the XAS at the pre-peak and on the second shoulder of the resonance slope which can also be explained by the influence of the pre-peaks that we got rid of by concatenating two very close measurement angles as described previously. The XMCD signal displays a slightly higher intensity for the lower temperatures, similarly to the Fe K-edge.

This experiment didn't highlight any noticeable effect of the temperature on the XAS measurement and XMCD, and therefore can't corroborate the existence of any structural or magnetic transition between room and low temperatures yet.

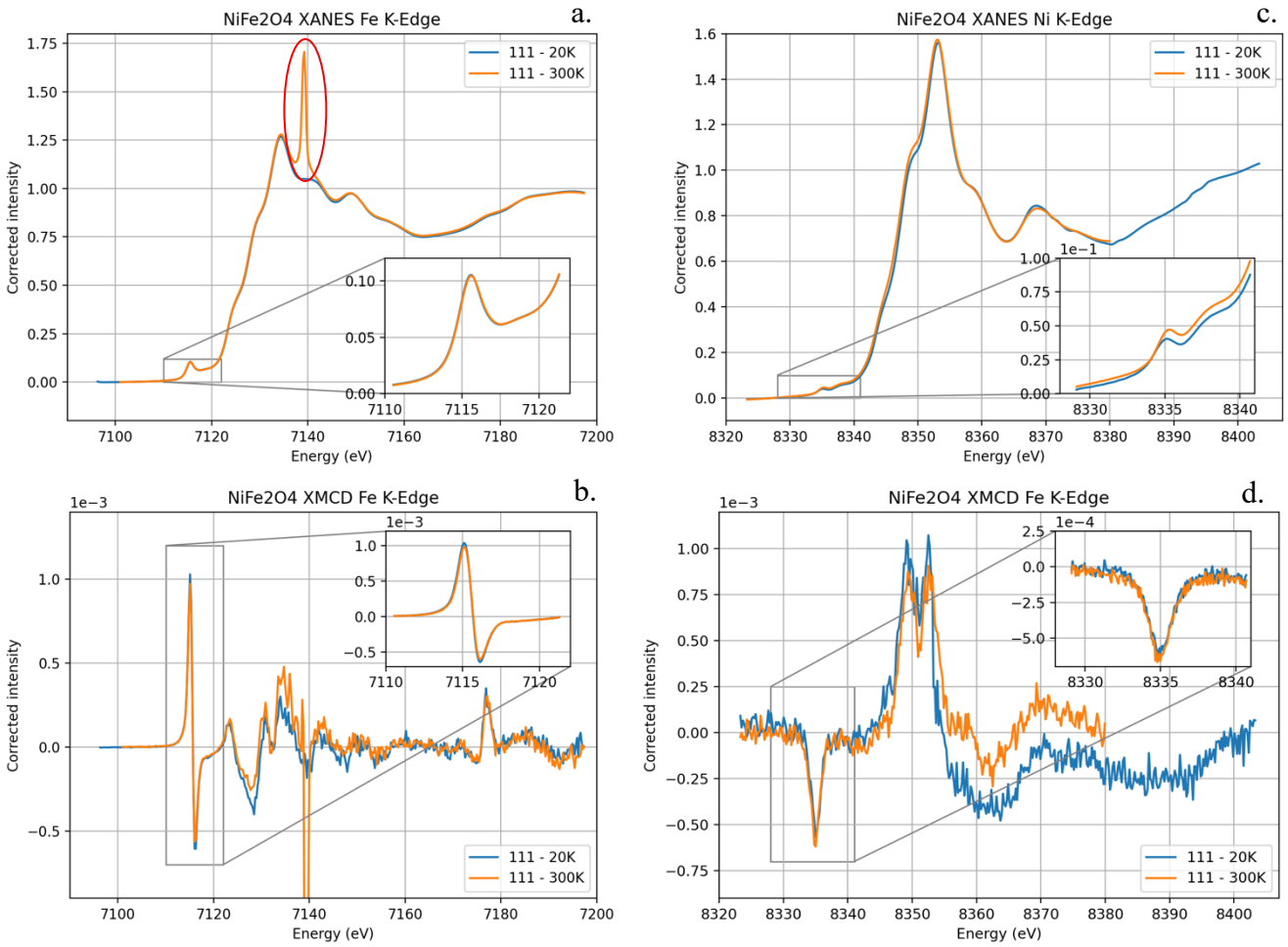

Figure 1: 300K and 20K measurements of the <111> crystallographic direction of NFO. (a) and (b) are the Fe K-edge XAS measurement and the corresponding XMCD. (c) and (d) are the Ni K-edge XAS measurement and the corresponding XMCD.

Figure 2 displays the crystallographic direction dependent XAS and XMCD measurements performed on the <111>, <110>, <100> plaquettes. As shown in panels (a) and (b), presenting respectively the evolution of the XAS and XMCD spectra measured at the Fe K-edges as a function of the crystallographic direction, there is a slight difference in the XAS pre-peak, <100> being more intense than the other directions. The XMCD displays a very clear direction dependance of the signal. <111> displays the strongest signal, <110> the intermediary and the <100> is the lowest but has a more spread shape. No clear difference at the main edge.

Panels (c) and (d) present the same measurements at the Ni K-edge. The XAS pre-peak is split in two bumps, The <111> direction shows a mixed behavior between the <110> which only has the first one and the <100> which only has the second one. The effect is even clearer on the XMCD signal which displays a gradual drop

of its intensity from <111> to <110> direction, and completely disappearing for the <100> direction. The effect on the main peak is different: <110> direction XMCD intensity is the lowest of the three directions, <100> being almost the same as <111>. The difference in intensity at the main edge and in the EXAFS can be explained by the presence of pre-peaks in the initial measurements, as previously explained.
This experiment highlighted a strong crystallographic direction dependance of the XMCD signal, noticeably at the pre-peak. Further studies and FDMNES calculations are necessary to fully understand the meaning of these features.

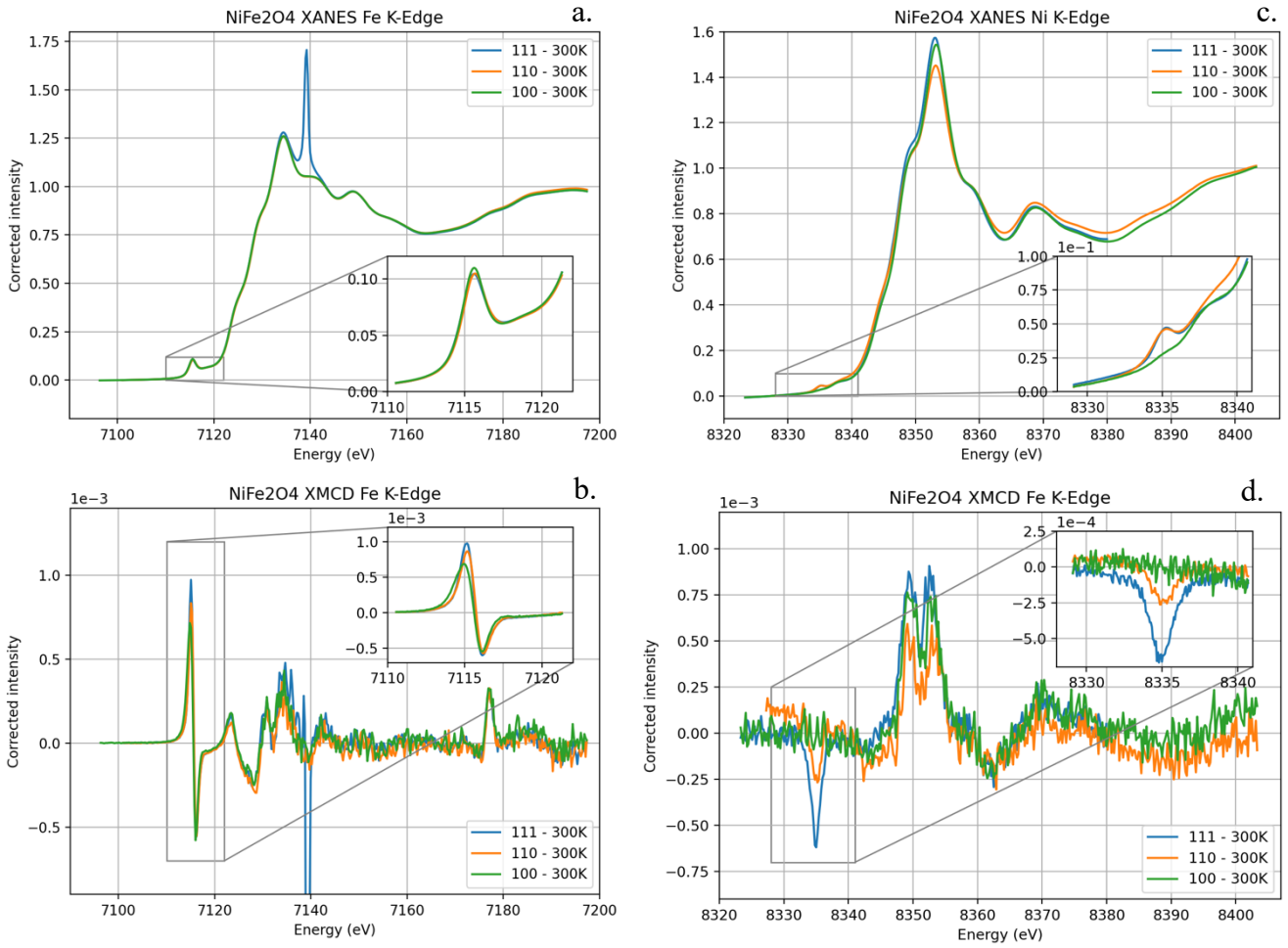

Figure 2: 300K XAS and XMCD measurements of the <111>, <110> and <100> directions. (a) and (b) Respectively shows the Fe K-edge XAS measurement and corresponding XMCD. (c) and (d) Respectively shows the Ni K-edge XAS measurement and corresponding XMCD.

Summary :

In summary we have obtained interesting results in $NiFe_2O_4$ consistent with the results on other synchrotron experiments that we performed in parallel. Through these measurements we confirmed that there was no noticeable modification of the signal with the temperature, as measured on BM02 – D2AM beamline during a RXD experiment. Another result is that at both Fe and Ni K-edges, the XMCD signal at the the pre-peak is drastically different in the <100> direction than the others. To conclude, this experiment failed to reveal the transition at 98 K reported in the litterature but brought insights on the anisotropy of the magnetic properties of NiFe2O4. Further FDMNES simulations and analysis will be conducted in order tu fully understand the nature of this anistropy. Additional X-ray diffraction measurements are also planned to confirm the absence of a structural distorsion as suggested here.

References: [1] J. K. Dey *et al., Phys. Rev. B* **99**, 144412 (2019)