EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal: *https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do*

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

fill in a separate form for each project or series of measurements.

type your report in English.

include the experiment number to which the report refers.

make sure that the text, tables and figures fit into the space available.

if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** X-Ray resonant diffraction : study of the thermal evolution of the orbital order in vanadium ferrite thin films	**Experiment number**: HC-5091
Beamline:	**Date of experiment**: from: 9/02/2023 to: 13/02/2023	**Date of report**:
Shifts:	**Local contact(s)**: Stéphane Grenier	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Main Proposer :
*Dr. LEFEVRE Christophe Inst. de Physique et Chimie des Matériaux de Strasbourg
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*Dr. GRENIER Stéphane Inst. Néel GRENOBLE CEDEX 9

Report:

Objective and expected results: Vanadium spinel oxide has been intensively investigated as one of the forefront topics in modern orbital physics and its potential benefits for new technologies. FeV_2O_4 (= FVO) is a unique compound since both Fe^{2+} and V^{3+} ions have orbital degrees of freedom, bringing about orbital-ordered states in the material. This orbital ordering can be retrieved by characterising the polyhedral distortions, for which the precise location of the oxygen atoms is crucial. While FVO's orbital ordering has widely been studied in bulk form, it has not been proven for thin films. However, precisely locating oxygen atoms in nanosized systems is a real challenge. The traditional strategies used for bulk samples fail in probing those with much less matter. Resonant Elastic X-ray Scattering (REXS) experiments in the Extended X-ray Absorption Fine Structure (EXAFS) domain have been proven successful in indirectly locating oxygen atoms in thin films. Therefore, we aim at using REXS-EXAFS to precisely locate oxygen atoms at different temperatures, in order to study the temperature evolution of the orbital ordering of FVO thin films.

Experimental :

Resonant Elastic X-ray Scattering experiments were perfomed on the D2AM beamline equiped with a cryofurnace. The ~ 40 nm thick FVO thin films samples, have been deposited by pulsed laser deposition either onto a $SrTiO_3$ (001) substrate or onto a MgO(001) substrates. They were placed inside a Be dome specimen holder evacuated down to 10^{-6} mbar (Fig. 1), and maintained to a fixed temperatures, between 300 and 20 K, by an ARS compressor. Some resonant diffraction spectra were acquired at the Fe K-edges, over the 7.070-7.370 keV energy ranges, for about different reflections chosen for their sensitivity to the positions of the oxygens in the cell, at 8 different temperatures (300, 200, 150, 120, 100, 70, 40, and 20 K). In addition, reciprocal space mapping of the 008 node have been made for each temperature.

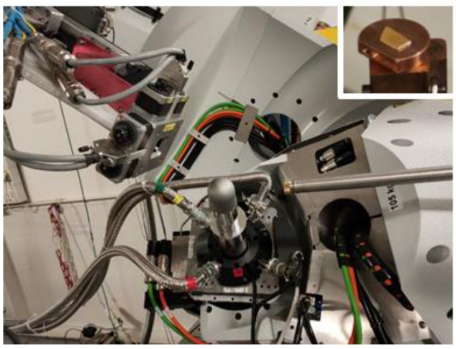


Fig. 1: Measurement configuration (the sample, in insert, is placed in an evacuated Be dome for the temperature dependent measurements)

Preliminary Results and Conclusions:

a) Structural transition a low temperature

We observed the splitting of the 008 node at low temperature for the FVO\MgO thin film (figure 2) which may be due to a cubic to monoclinic transition. This structural transition, which had not been evidenced up to now, seems to occur alongside the already-knozn magnetic transition in our material. This splitting has not observed for the FVO\STO thin film. The study of the different RSM will allow us to compute the unit cell parameters of this new structure.

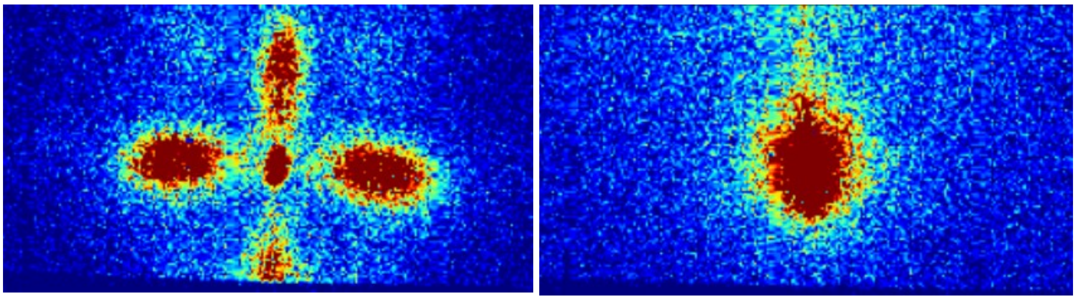


Figure 2 : RSM of the 008 node at T = 20K (left) and at T = 150K (right)

b) Recorded REXS spectra

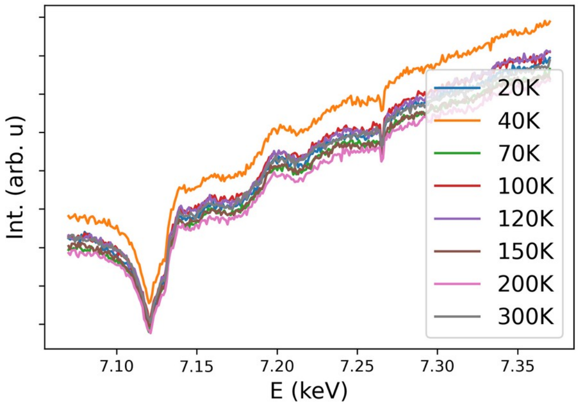
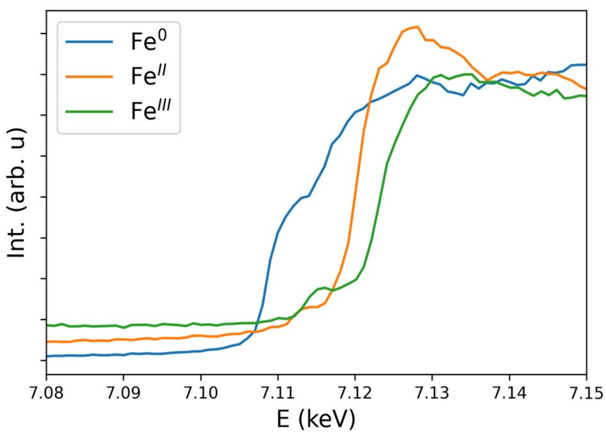


Figure 3 : REXS spectra of the 115 node of FVO\STO

REXS spectra were recorded for all the samples at different temperatures. As an illustration, some of the experimental spectra acquired for various temperatures, at the Fe K-edges for the *115* reflection of FVO\STO are shown in the figure 3. The signal is probably partly absorbed by the Be dome but one can however clearly observe distinct features on the spectra. The spectra will be fitted with the FitREXS and FDMNES codes, in order to determine the cationic distribution within the two cationic sites, and the positions of the anions for each temperature. After a long analysis procedure, the large set of data should thus give conclusions on the positions of the atoms, and therefore on the possible temperature-dependent lattice distortions. This will reveal whether the material posseses an orbital ordering in the thin film form or not, as well as its evolution whitin temperature.

c) determination of the oxidation state



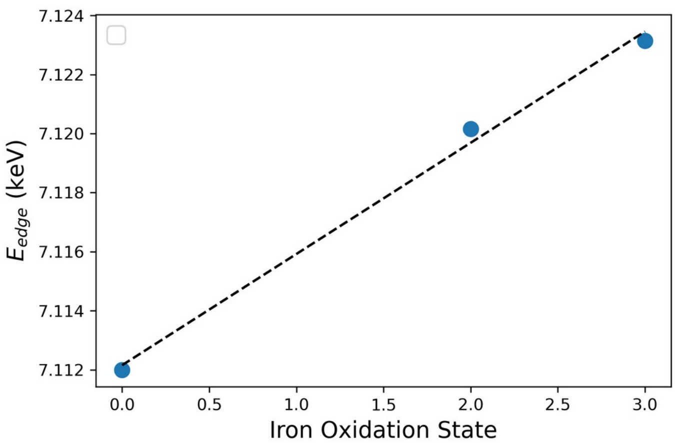


Figure 4 : (left) : Fluorescence spectra of three selected iron standart and (right) : plot of the edge as a function of the oxidation state.

The fluorescence of three standards was recorded in order to evidence the iron oxidation state in the different characterised samples (figure 4 left) . Those were metallic iron (Fe^{0}), ferrous oxalate (Fe^{+II}) and hematite (Fe^{+III}). The first analysis of theses spectra allows to draw up the iron oxidation state as a function of the edge (figure 4 right). This graph will be essential for the determination of the iron oxidation state in the different studied thin films.