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:** Local Structure in TiOF	**Experiment number**: HC4081
Beamline: ID11	**Date of experiment**: from:24/02/2021 to: 25/02/2021	**Date of report**: 09/08/2023
Shifts: 3	**Local contact(s)**: Jon Wright	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

James Cumby, University of Edinburgh

Scott Rait, University of Edinburgh

*Jon Wright, ESRF

Report:

TiOF adopts a tetragonal rutile structure, with O and F anions randomly distributed across the anion positions based on average (Bragg) crystallography. However, a local *fac*- anion arrangement within TiO_3F_3 octahedra is expected based on chemical bonding arguments, with a resulting off-centring of Ti^{3+} cations from their ideal positions. This has previously been reported in FeOF [1] but our initial laboratory results showed that TiOF adopts a different anion arrangement.

The aim of this experiment was to measure and interpret the diffuse X-ray scattering from TiOF, taking advantage of the combination of high flux, high energy and large dynamic range available at ID11. By combining direct modelling of diffuse scattering features with corresponding real-space analysis (3D-ΔPDF) we expected to determine the correlated displacements of Ti cations within the structure.

Due to the continuing pandemic, it was necessary to tailor our experimental approach in order to run the experiment remotely. Four different crystals were mounted, and measurements taken using a variety of X-ray fluxes, rotational speeds and image collection times. Crystals 1 and 3 were only weakly scattering due to the small size of the crystallites, meaning that only Bragg scattering was observed. Crystals 2 and 4 both showed transverse-polarised rods of diffuse scattering along [110] directions, consistent with 2D ordered correlations between Ti displacements. For crystal 4, variable temperature measurements were additionally used to establish the temperature dependence of this diffuse scattering (Fig. 1A). The diffuse intensity decreased slightly with increasing temperature, demonstrating that the diffuse scattering occurs due to static disorder rather than thermal excitations (phonons).

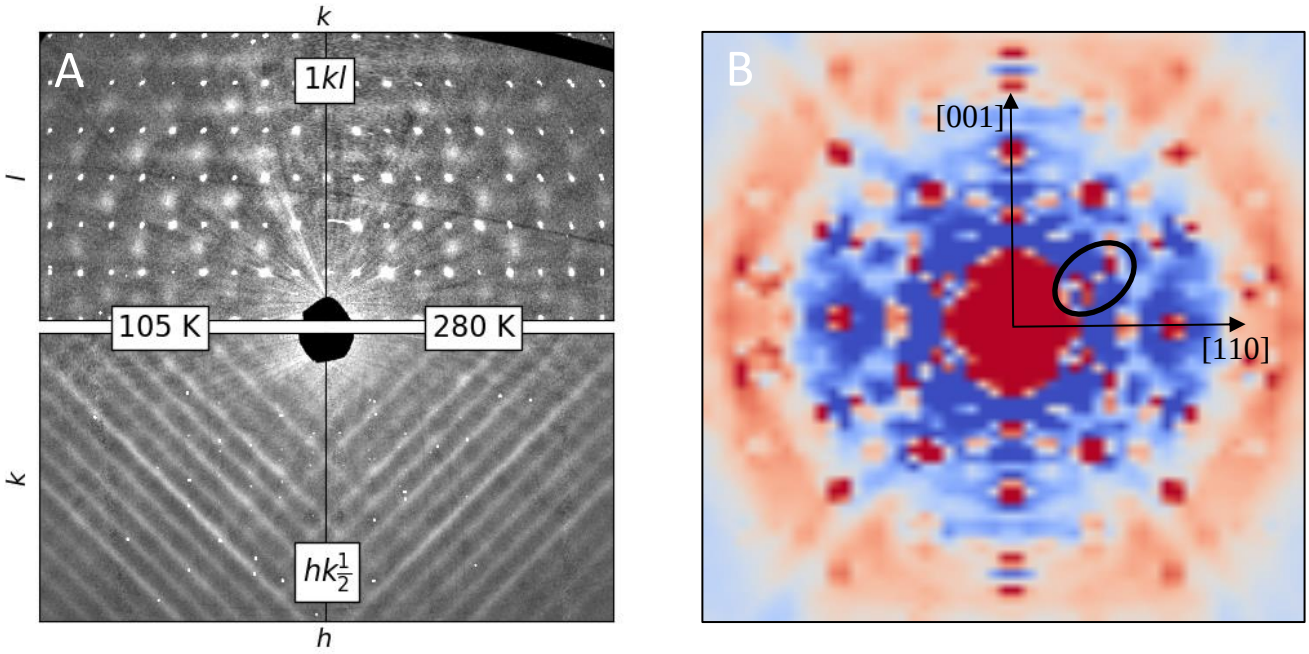

Figure 1: (A) Reconstructed precession images of [1kl] (top) and [hk0.5] (bottom) crystallographic planes showing rods of diffuse scattering along (110) directions. Data collected at 105 K (left) and 280 K (right) show a slight reduction in diffuse intensity consistent with static correlated disorder. (B) 3D-ΔPDF through the real-space (110) plane showing displacements of neighbouring Ti cations. The highlighted region shows strong correlations between Ti atoms separated by a translation of [0.5,0.5,0.5].

As expected, the diffuse scattering from TiOF differes from that observed for FeOF (i.e. parallel displacements of cations between edge-sharing octahedra) and is instead consistent with anti-parallel displacements of Ti cations within edge-sharing octahedra. However, the data do not agree with a simple model expected from edge-sharing *fac*-TiO_3F_3 octahedra due to the systematic absence of some of the diffuse rods.

Using the measured data, we have been able to obtain a 3D-ΔPDF representation of the scattering (Fig. 1B). This has been complicated due to inconsistencies between background and sample measurements, but allows us to observe the real-space distortions from the average (Bragg) structure. A key finding from the 3D-ΔPDF is that Ti atoms separated by a real-space translation of (0.5,0.5,0.5) (highlighted in Fig. 1B) show strong correlations. This is inconsistent with uncorrelated order between perpendicular (110) planes and is indicative that the scattering occurs from multiple, lower symmetry, domains.

Currently, no distortion model can simultaneously match both the observed scattering and 3D-ΔPDF results. Work is on-going to understand the measured scattering using a combination of modelling techniques and *ab initio* simulations.

[1] Brink, F.J, Withers, R.L. and Norén, L., *J. Solid State Chem*. 161, **2001**, 31.