

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://www.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 from 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.



	Experiment title: High-pressure NTE in niobium oxyfluoride at low temperature	Experiment number: CH6141
Beamline: ID15B	Date of experiment: from:01/02/2022 to: 04/02/2022	Date of report: 11/09/2023
Shifts: 3	Local contact(s): Michael Hanfland	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): James Cumby, University of Edinburgh Dr Claire Hobday, University of Edinburgh Eliza Dempsey, University of Edinburgh		

Report:

NbO_2F adopts the ReO_3 -type structure which offers vibrational flexibility due to corner-sharing octahedra. This structure commonly exhibits low- or negative-thermal expansion (NTE) due to these vibrations which lead to a net reduction in volume during heating. NbO_2F itself exhibits positive thermal expansion which appears to approach a maximum near to room temperature., in contrast to TaO_2F which exhibits near-zero thermal expansion, despite having very similar unit cell parameters and ionic radii.

Another feature of the ReO_3 structure, also linked with octahedral flexibility, is that it often transforms to a rhombohedral polymorph under moderate pressures (0.7 GPa and 0.4 GPa for TaO_2F and NbO_2F , respectively^{1,2}). These two effects compete with each other in some way, such that NTE requires volume-reducing vibrations to be substantial at moderate temperatures, but not so prevalent that the structure is more stable in a rhombohedral phase.

The aim of this experiment was to measure the thermal expansion and phase transition behaviour of NbO_2F under varying pressure and temperature conditions in order to determine how these two effects interact throughout the temperature/pressure phase diagram. During the experiment, it was also possible to measure an additional fluorine-doped sample ($\text{NbO}_{1.9}\text{F}_{1.1}$) for comparison.

Technical limitations around maintaining a relatively low pressure (< 1 GPa) while changing temperature meant that it was experimentally challenging to access all of the P/T points originally proposed, and it was not possible to measure different temperatures at identical pressures. The phase transition into the rhombohedral phase was also kinetically slow at these temperatures, meaning that a coexistence of rhombohedral and cubic phases was frequently observed. Despite these challenges, however, using careful diffraction analysis using Pawley and Rietveld fitting we were able to determine the evolution of the phase transition with temperature (Fig. 1).

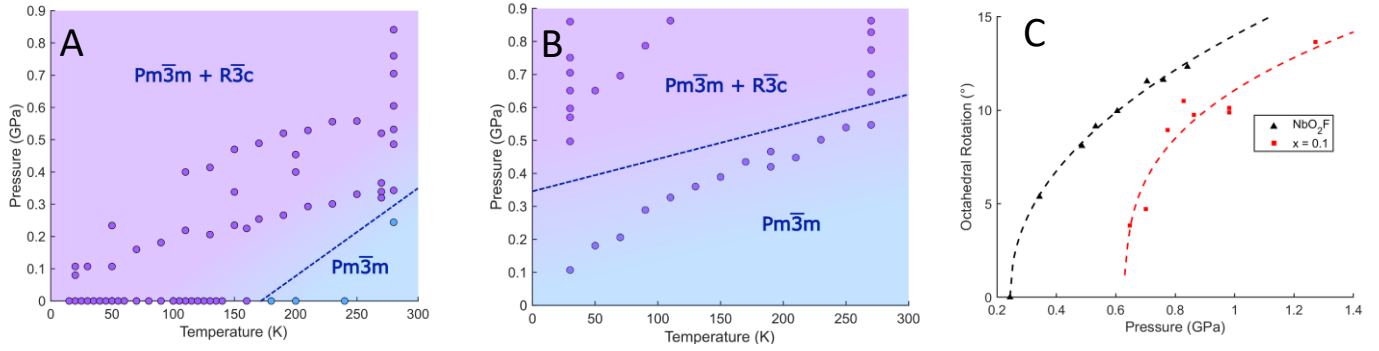


Figure 1: Evolution of the cubic-to-rhombohedral phase transition with temperature and composition in $\text{NbO}_{2-x}\text{F}_{1+x}$. (A) Pressure-temperature phase diagram for NbO_2F showing a reduction in phase transition pressure on cooling; (B) P-T phase diagram for $\text{NbO}_{1.9}\text{F}_{1.1}$ showing that the rhombohedral transition is much less sensitive to temperature; (C) Order parameter fits to the phase transition at 270 K (determined via Rietveld refinement) showing that $\text{NbO}_{1.9}\text{F}_{1.1}$ exhibits a higher critical pressure than NbO_2F .

Our results find that in both NbO_2F and $\text{NbO}_{1.9}\text{F}_{1.1}$ the transition to a rhombohedral phase occurs with pressure, but this critical pressure is lower for the NbO_2F sample (Fig. 1C). On cooling, this critical pressure drops for both materials. For NbO_2F we find evidence for the formation of a rhombohedral phase on cooling which has not previously been observed; neutron diffraction experiments are scheduled to investigate this subtle effect further. For the fluorine-doped sample, we see no evidence of a transition down to the lowest temperature measured (30 K).

Based on the temperature/pressure points measured, we were able to fit a combined temperature-pressure-volume equation of state (Fei-type thermal dependence and second order Birch-Murnaghan pressure dependence, Table 1). The results for the two compositions look very similar (within error) except for the thermal expansion terms α_0 and α_1 (the linear and quadratic temperature coefficients relative to 280 K). NbO_2F has a larger linear dependence on temperature, which is consistent with a more positive thermal expansion behaviour. Interestingly, however, the quadratic terms (α_1) show opposite signs for each composition. A positive α_1 term could be important in understanding the origin of NTE in ReO_3 -type materials, therefore computational modelling is on-going to better understand this behaviour.

Table 1: Results from fitting a P-V-T equation of state to refined volumes for each composition.

Composition	V_0 (\AA^3)	α_0 (10^{-6} K^{-1})	α_1 (10^{-8} K^{-2})	α_2 (K)	K_0 (GPa)	dK/dT (GPa K^{-1})
NbO_2F	60.71(14)	180(30)	-33(17)	-0.13(6)	10.6(7)	-0.001(6)
$\text{NbO}_{1.8}\text{F}_{1.2}$	61.54(14)	71.65(5)	54(22)	-0.04(10)	11.1(4)	-0.019(3)

The results obtained from this experiment have demonstrated that NbO_2F -like materials become more likely to undergo a transition to a rhombohedral phase upon cooling. In particular, work is on-going to investigate a previously unseen temperature-driven transition in NbO_2F . Fluorine substitution in NbO_2F appears to increase this transition pressure as well as reducing its temperature sensitivity.

These results are currently underpinning a larger study on the thermal expansion behaviour in fluorine-doped NbO_2F materials. Currently these results have been presented at peer-reviewed conferences (IUCR, ISNTE) but we expect they will form the basis of one or more publications in this area shortly.

[1] Carlson, S. *et al.*, *Acta Cryst. B*, **2000**, 56, 189.

[2] Cetinkol, M. *et al.*, *J. Phys. Chem. Solids*, **2007**, 68, 611.