EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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:** Investigation of phase transitions and melting/recrystallization dynamics in elemental Selenium under presssure with controlled fast heating/cooling rates.	**Experiment number**: HC-4431
Beamline: BM23	**Date of experiment**: from: 08/06/2021 to: 14/06/2021	**Date of report**: 16/10/2021
Shifts: 18	**Local contact(s)**: Joao Elias Figueiredo Soares Rodrigues	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Studies of disordered (amorphous or liquid) materials under pressure is a field of research with strong interdisciplinary implications, ranging from basic condensed matter physics to geophysics, environmental and applied sciences. Among many covalent systems, the peculiar phase behavior of pure elemental Se has attracted large attention as an interesting simple model system for examining the pressure effects on the stable and metastable phases, because of the wide range of structural and bonding properties shown by the crystalline and non-crystalline forms of the elements. However, regardless of the large efforts over the years, phase behavior of this simple elemental substance is still poorly understood. For example, even though a semiconducting to metallic transition has been observed in the liquid phase, associated changes in the density and local structure is not yet known. Thinking that Se is the only easily vitrified elemental substance (cooling rate 20 K/min), several fundamental questions will arise: (i) how will be the dynamics of melting and crystallization under high pressure? (ii) will it be possible to achieve direct amorphous to liquid transition (very rare phenomenon for elemental systems) and liquid to amorphous vitrification bypassing the crystallization with enough rapid heating/cooling rates?(iii) are there any differences between the amorphous structures quenched at different pressures (polyamorphism)? Phase transitions of elemental Se are far to be simple even at room temperature conditions. High pressure x-ray diffraction experiments on the amorphous Se often give controversial results, values of resistivity measurements (more than 10 studies in literature, see ref.) differ several orders of magnitude at similar pressures.

The goal of our project was twofold: firstly, we have aimed to study local structure liquid Se under pressure in order to identify possibly structural anomalies in the liquid and amorphous phases. An important motivation of the experiment was also to study the pressure effects on the melting-recrystallization dynamics. Secondly, we also aimed to study the structural changes occurring in the amorphous phase from a local structural point of view. For this purpose, we have used x-ray absorption spectroscopy (XAS), an ideal probe of local structures in disordered systems. We have performed a series of high pressure EXAFS experiments in the BM23 beamline on elemental Selenium, both under high temperature and room temperature conditions. A home-made resistively heated diamond anvil cell (DAC) system from the users group was nicely adopted on the BM23 micro-XAS

station (See Fig.1). The resistively heated cell and also the normal design diamond anvil cells (for cold compression experiments) were equipped with nanopolycrystalline diamond (NPD) anvils to achieve glitch free EXAFS data. EXAFS spectra and single energy x-ray absorption temperature scan (SEXATS) data have measured along several quasi-isobaric heating cooling runs acceding the melting lines (Fig.2). Features of XAS and SEXATS data have shown clear evidence of amorphous-crystal-liquid transitions. It was noticed that at pressure above 2.5 GPa, recrystallization temperature from the liquid (or undercooled liquid) was decreased, and almost very near to vitrify again the amorphous Se again under high pressure. However, when we quickly heated up the sample at a high temperature, the hot molten sample went out from the sample chamber because of the gasket failure (possibly related with chemical reactions). The cell was opened for reloading the sample, unfortunately, one of the glued diamonds was detached from its seats and the seat (made out of TiB_2) was cracked (surprisingly, the anvil was safe). In these circumstances, we were not able to load a new sample for continuing the experiment starting from the above interesting and crucial point (2.5-3 GPa). Already obtained HP-HT data is of enough quality for refinements and can provide new local structural information concerning the liquid-Se under pressure and structural changes along the amorphous-crystal-liquid (possibly also supercooled liquid) transitions. However, in order to publish data in a good quality journal, further measurements at the remaining pressure -temperature and heating/cooling conditions will be needed. Therefore, a proposal application for continuing the present project is foreseen.

At the remaining beamtime, we have performed cold compression experiments on amorphous Selenium under different degrees of hydrostaticity exceeding 30 GPa. Combined EXAFS and XRD data have been measured along three runs with [Ne and methanol:ethanol mixture] or without pressure transmitting mediums (Fig. 3). Such a systematic measurement was never performed and long has been desired to resolve the controversial results in the existing literature. On the other hand, high pressure phase behavior of amorphous Se has never been studied at pressure above 10 GPa. As can be seen from Fig.3, EXAFS and XRD data show different trend of with increasing pressure, implying that phase behavior of Se is more complex than previously known, being highly sensitive to hydrostatics and experimental conditions, explaining the reason of the scares diffraction and resistivity data in the literature. Measured HP EXAFS data is of exceptional quality (especially along run-1 and run-3). However, an issue with the data is a distortion of the background introduced by the $L_{2,3}$ absorptions edges of the Pt mirrors (of the KB system). We overcame this issue by introducing a fake double electron excitation feature within the refinement scheme of the GNXAS method. As a result, we could perform highly reliable refinements on extended k-range, as shown in Fig. 4. Analysis is going on and partially completed (Fig. 5). Our experiment and analysis provide a very different perspective for understanding the structural transitions in amorphous Se at different length scales (short, intermediate and long range). Results will significantly improve the current knowledge on the Se. A manuscript is also under consideration and expected to be completed and submitted to a good quality journal in near future.

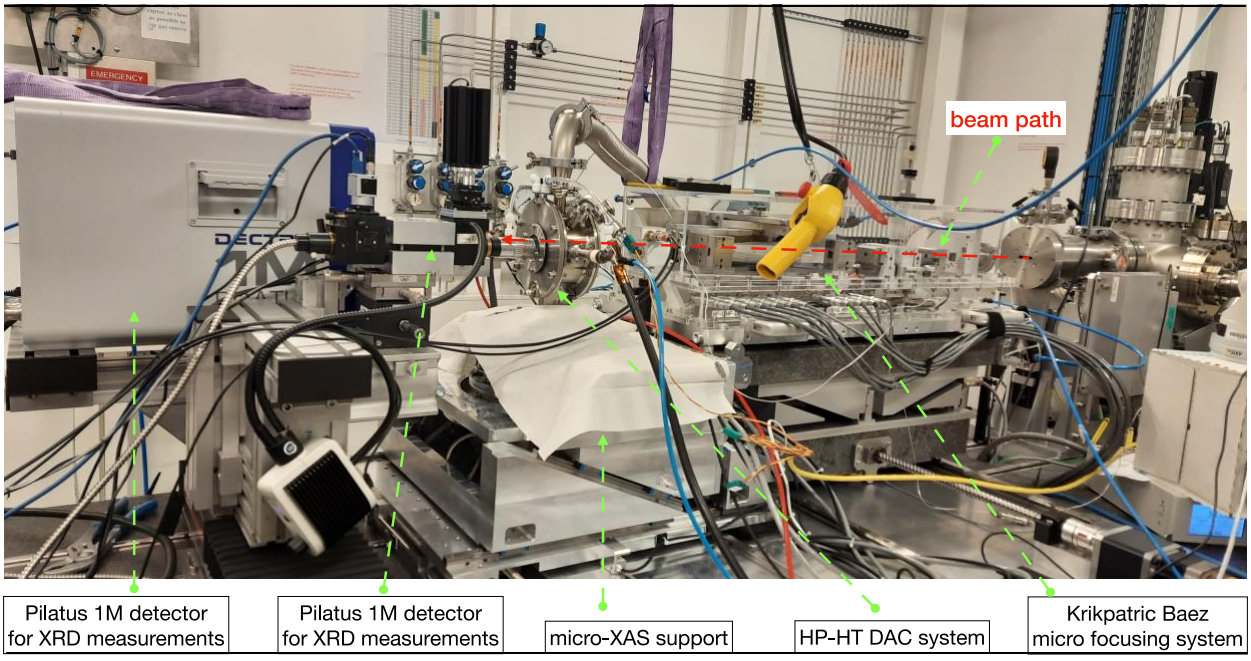

Fig. 1 *BM23 High pressure exprimental setup coupled with the resistively heated diamond anvil cell.*

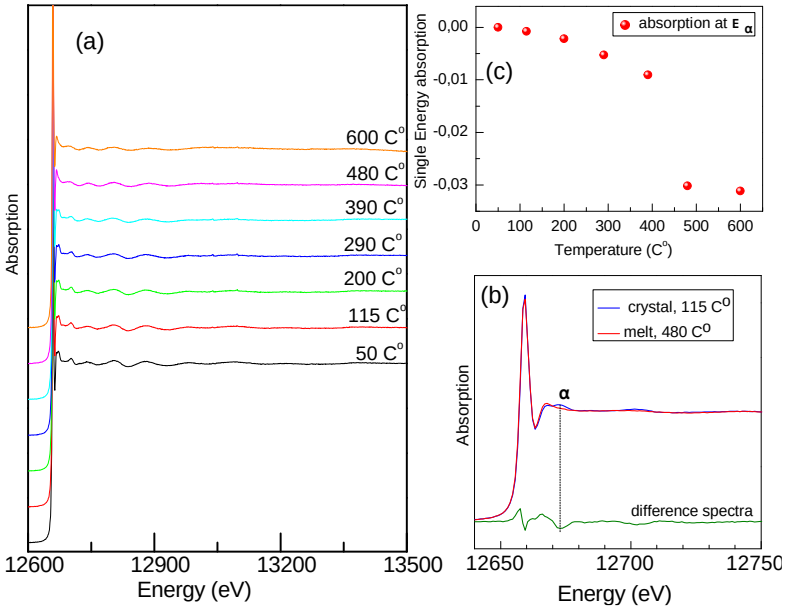

Fig. 2: *(a) selected XAS data measured along an isobaric heating run at 2GPa. (b) XANES data measured at two different temperatures and their difference showing a minimum around E_a. (c) Temperature dependence of the absorption at single energy E_a.*

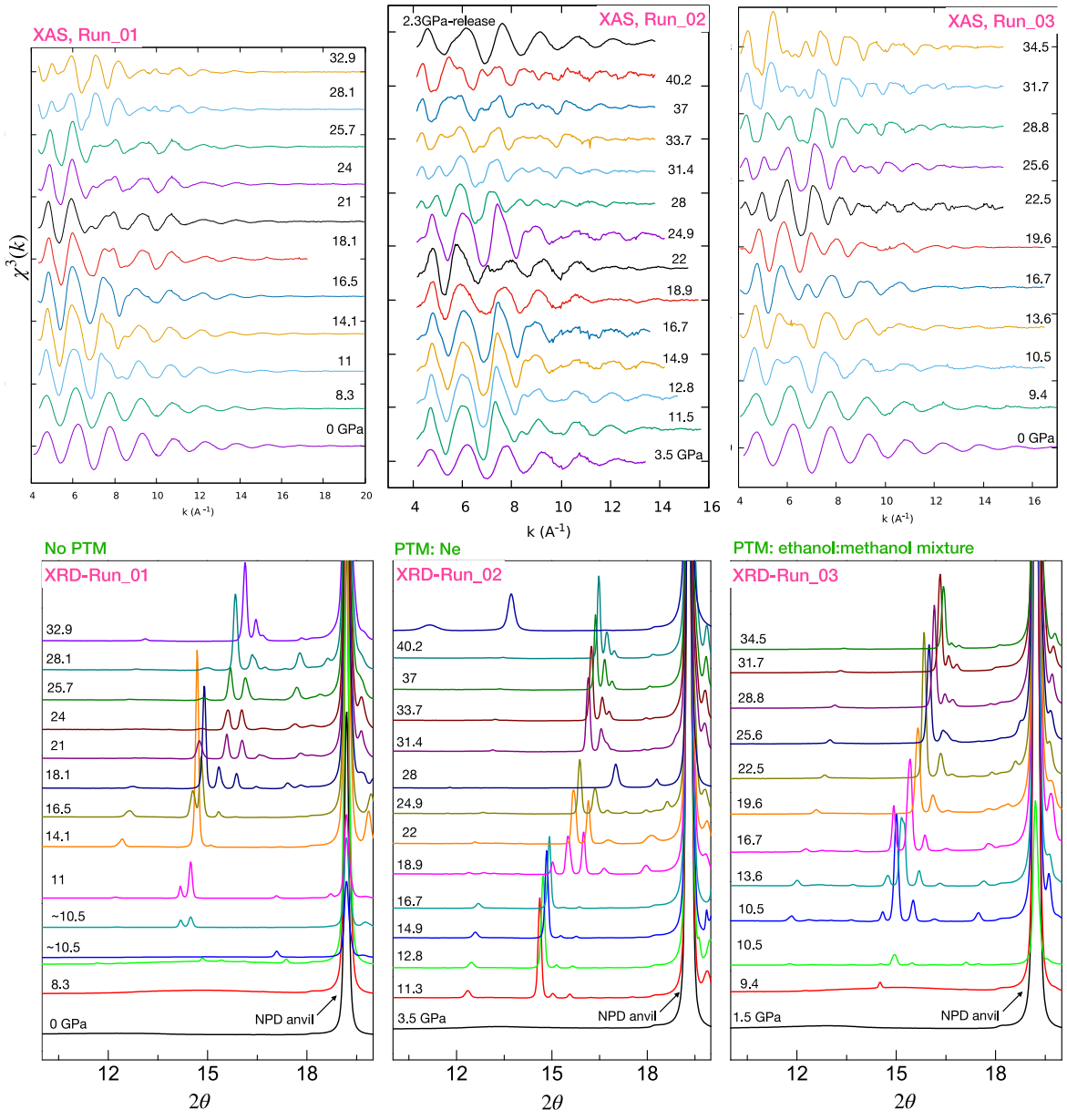

Fig. 3 *Combined EXAFS and XRD data measured along three different runs.*

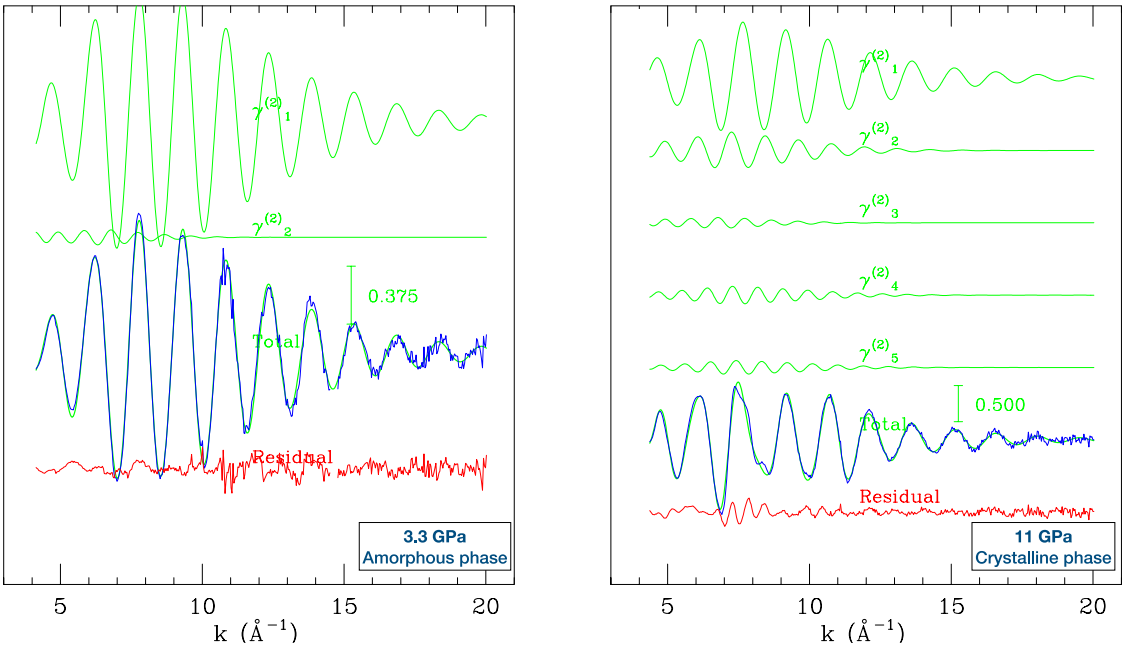

Fig. 4 *Example of EXAFS fitting (with GNXAS package) at two different pressures and phases (amorphous and crystal).*

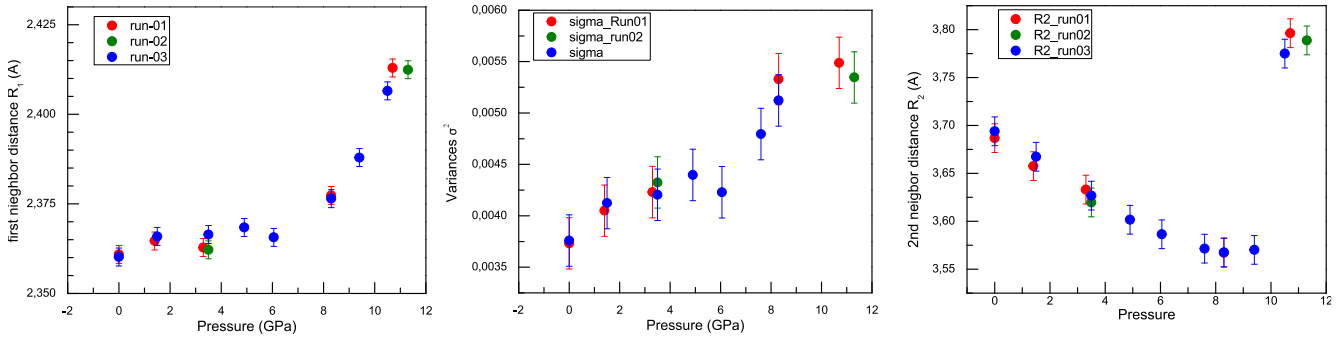

Fig. 5 *Preliminary EXAFS fitting results. Pressure depences of first neighbor distance* $\boldsymbol{R_1}$*, variances* $\boldsymbol{\sigma^2}$ *and second neighbor distance* $\boldsymbol{R_2}$ *(in the same chain of Se atoms) up to the crystallization onset (P~10.5 GPa).*