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.

	Experiment title: Investigation of the local structural changes in glass under ultrahigh pressure	**Experiment number**: HC-4645
Beamline:	**Date of experiment**: from: 03/11/2021 to: 09/11/2021	**Date of report**: 04/02/2022
Shifts:	**Local contact(s)**: Joao Elias Figueiredo Soares Rodrigues	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Experimental studies of ultra-high pressure (P>1 Mbar) polyamorphism in the covalently bonded network forming amorphous systems has long been a challenging topic. There is not yet enough experimental data for convincingly describe the densification and evolution of local structures in the common simple amorphous materials including SiO_2 and other geophysical relevant disordered systems under ultrahigh pressures (e.g., conditions in the deep Earth). In this project, we have aimed to investigate the densification and evolution of local structures in the simple network forming glasses under ultrahigh pressures exceeding 150 GPa using $GeSe_2$ as the model system using x-ray absorption spectroscopy (XAS), a technique ideally suited for the studying the local properties of disordered systems. $GeSe_2$ is a particular network forming glass from the XAS technique point of view, allowing to probe both cation (Ge) and anion (Se) local sites along the same compression run. Such experimental data enable us to perform double edge EXAFS refinements on extended k-range yielding more accurate quantitative local structural information.

We have planned the beam time for measuring two separate runs. The first run was planned for a target pressure of 150 GPa. The sample for this run was loaded without pressure transmitting mediums (PTM) due to practical reasons and also to avoid possible infiltration of the gas PTMs into the glass structure. The second compression run was planned for a target pressure of about 50-60 GPa, for a sample loaded with Ne as PTM in order to investigate the possible effects of such PTMs. Diamond anvils were equipped with nano-polycrystalline diamond (NPD) anvils to obtain glitch free EXAFS data.

During our beam time, nearly 3 days of intervention was necessary to solve the problems related with the accelerator tunnel. However, using the remaining 9 shifts of beam time, we could successfully measure a complete set of EXAFS data scanning through both Ge and Se K-edges, reaching ~160 GPa. Pressures in this experiment were calibrated by measuring the XRD patterns of gold. XRD patterns were collected also for the $GeSe_2$ glass for monitoring the sample states (amorphous or crystal). No evidence of crystallization was observed.

The complete set of XAS data are reported in Fig. 1. As far as we know, this is possibly the first double-edge EXAFS measurement that has been performed exceeding Mbar pressure range. Quality of the EXAFS data is quite good thanks to the excellent performance of the BM23 beamline setup.

As shown in Fig.1 and Fig.2, XANES range shows very obvious changes, indicating large structural modifications both in the short and medium range ordering under pressure. An interesting feature of pressure dependent changes in the XANES range is the clear shift in the edge energies, which show a two-step process. A large redshift of Ge K-edge (2 eV at 100 GPa) and opac sample colour at higher pressures are the solid evidence of a gradual band gap close along a semiconductor to metallic transition of the GeSe2 glass. Interestingly, energy shifts at the Ge and Se K-edges show different trends (red shift at the Ge K-edge and blue shift at the Se K-edge). We are currently performing molecular dynamics simulations for understanding the exact origin of such a behaviour in the XAS data.

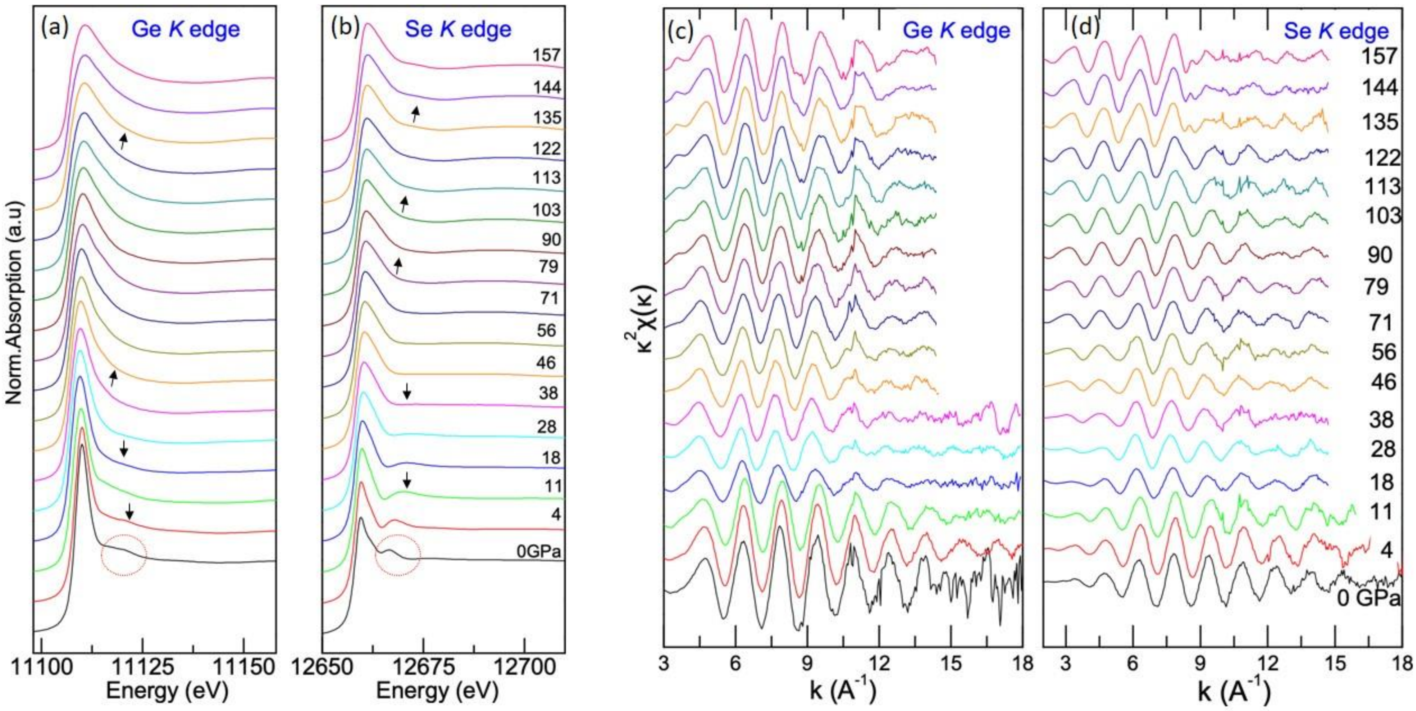

Fig. 1, Ge and Se K-edge XAS data measured at different pressures up to 157 GPa. (a,b): XANES part of the data (c,d): Extracted experimental EXAFS from the high pressure XAS data.

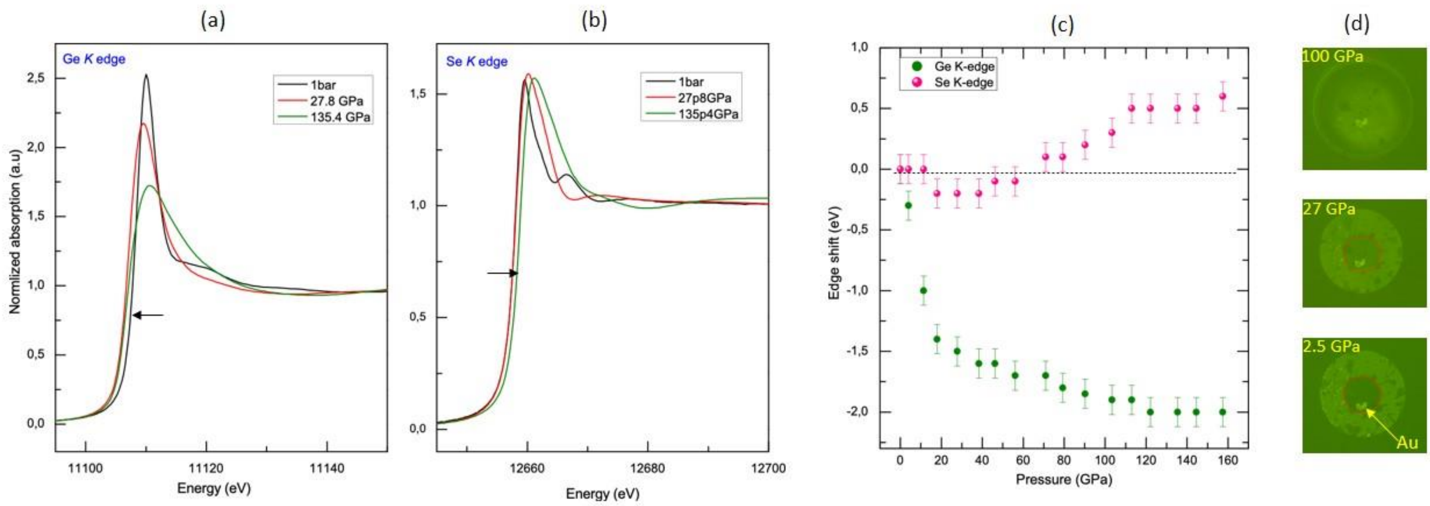

Fig. 2, (a,b): Ge and Se K-edge XA NES data for selected pressures (c): pressure dependent energy shift of Ge and Se K-edges. (d) optical image of the sample at selected pressures.

Preliminary double-edge EXAFS experiments have also been performed using the GNXAS method. In Fig.3, we report an exemplary double-edge refinement performed for P=4.0 GPa. As it can be seen, the agreement between the theoretical and experimental signals are perfect thanks to the ability of the GNXAS method for taking into account the effects of double-electron excitation channels and also the artifacts introduced by the Pt mirrors (of the KB system) in this pressure range.

Because of the large correlations between the fitting parameters, we are currently performing molecular dynamics simulations as well for having a guide for more careful and accurate refinement of the complete set of high quality EXAFS data that we have obtained during our beam time. By advanced experimental and theoretical methods, we expect reliable quantitative local structural information for describing the pressure induced densification mechanisms in GeSe2 glass and similar systems. We expect to publish a good quality article that can be referenced for the future studies in the field.

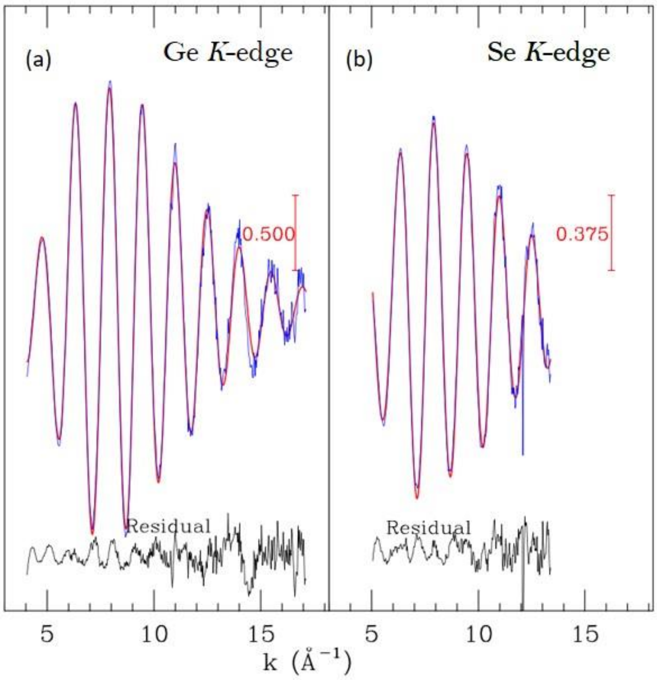

Table. 1, structural parameters obtained from a preliminary double edge fit

CN_{Ge}	CN_{Se}	$R(Å)$	$\sigma(Å^{-2})$
3.93	2.18	2.342	0.0045

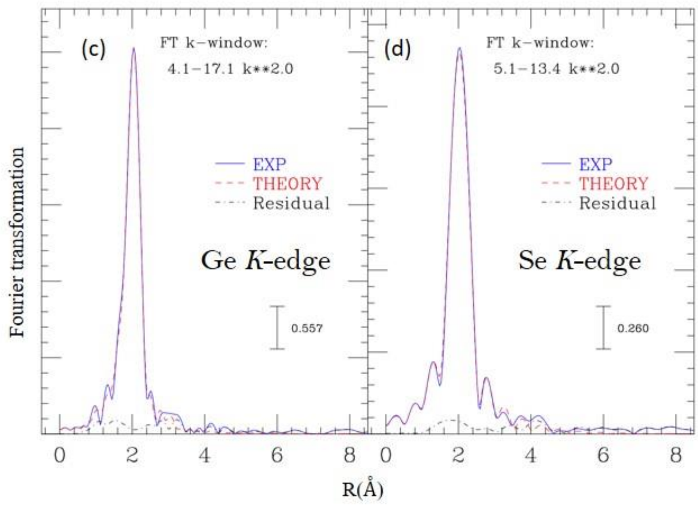

Fig. 3, (a,b): An exemplary preliminary double-edge (Ge and Se K-edges) EXAFS fit for P GPa.
(c,d): Fourrier transformation of the experimental and theoretical Ge and Se K-edge EXAFS signals