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:** **Detailed examination of the pressure induced martensitic transition in xenon**	**Experiment number:**
Beamline: ID15B	**Date of experiment:** from: 16/09/2020 to: 20/09/2020	**Date of report:** 29/03/2022
Shifts: 13	**Local contact(s):** Gaston Garbarino	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Angelika D. Rosa[1*] (PI), F. Zecchi[1], Joao E. F. S. Rodrigues[1*], E. Mijiti[1*], O. Mathon[1*], T. Irifune[2], N. Ishimatsu[3], A. Dewaele[4*]

[1] European Synchrotron Radiation Facility, Grenoble, France

[2] Geodynamics Research Center (GRC), Ehime University, Matsuyama 790-8577, Japan

[3] Graduate School of Advanced Science and Engineering, Hiroshima University 1-3-1 Kagamiyama, Higashihiroshima, Hiroshima 739-8526, Japan

[4] CEA, DAM, DIF, 91297 Arpajon Cedex, France

Report:

The main objective of this project was to investigate the underlying mechanism of the martensitic fcc to hcp transition and the thermoelastic properties of xenon in a wide pressure and temperature domain (90 GPa and 1200 °C). Due to their simple electronic configuration, noble gases are excellent model systems with important implications in solid state Physics, Materials and Earth sciences [1-3]. We have recently investigated the stability fields and equations of state of fcc/hcp argon, krypton and xenon at room temperature and up to 150 GPa using X-ray absorption and X-ray diffraction techniques [4, 5, 6]. Under high temperature, experimental data are presently sparse and have been limited to laser-heating techniques, with unavoidable temperature gradient issues [7]. They are however essential to constrain the mechanism of the martensitic transition. In addition, the thermoelastic parameters for heavy noble gases are little constrained [8], but are essential to expand theoretical models and to refine existing data on noble gas solubilities in the deep Earth's mantle phases [9].

We have characterized the martensitic transition mechanism and its effect on the thermoelastic properties of solid xenon up to 60 GPa and 500 °C using XRD and XAS measurements in a resistively heated diamond anvil cell (RH-DAC). The RH-DAC provides a homogenous heating and therefore permits to monitor the transition progress and crystallographic properties of the sample in a continuous manner and with high precision.

ID15B experiment:

The diffraction experiments were carried out at the beamline ID15B of the ESRF (**Fig. 1, left**). The Eiger 9M detector was not available at the time of the experiment and the MAR Research 345 mm Image Plate (MAR345) was therefore employed. The X-ray beam was tuned to an energy of 30.17 keV (corresponding to a wavelength of 0.411 Å) and was focused to a spot size of 10*10 μm^2 in the horizontal and vertical directions. The sample to detector distance was set to 399 mm and calibrated using an Si standard, similar to detector tilt and rotation parameters.

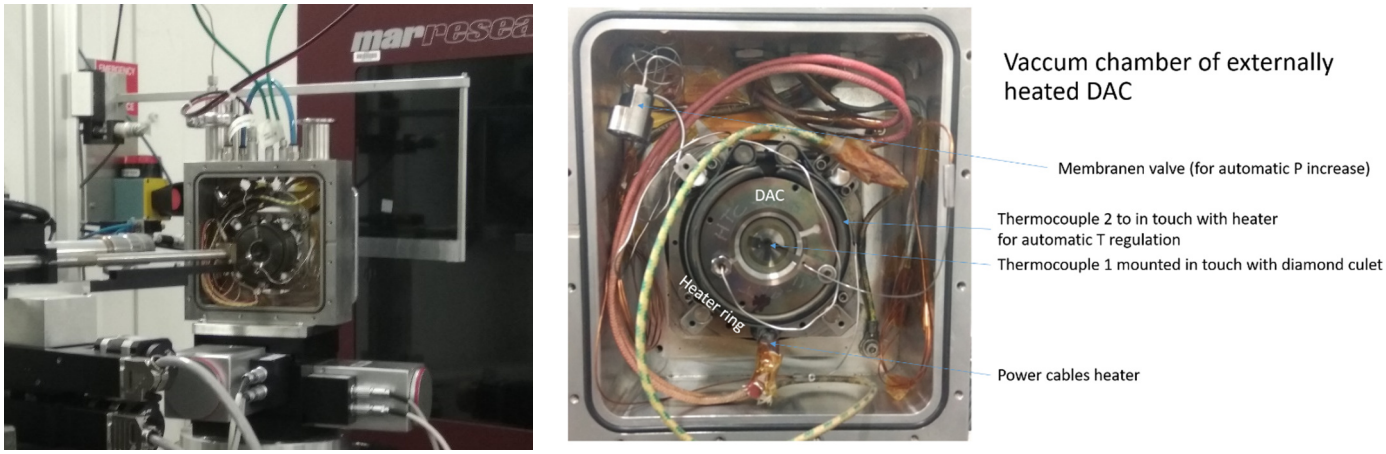

Fig. 1. *Experimental setup at the diffraction beamline ID15b and RH-DAC employed in this study.*

For high pressure generation three membrane driven diamond anvil cells of the Letoullec design were employed provided by the ESRF sample environment. The diamond anvil cells were equipped with single-crystal diamonds of the Boehler-Almax design with culet sizes of 250 and 300 µm. Xenon was loaded in the sample chamber using high-purity xenon from Messner and the gas loading device at the ESRF. For high temperature generation the externally heated diamond anvil cell developed at the ESRF sample environment was employed that allows reaching maximal 600 °C. Three isothermal high-pressure runs were performed at 155, 295 and 455 °C and up to 60 GPa. The pressure was determined from the lattice parameter of a small gold chip (5*5*5 µm^3), the sample temperature measured on the table of one diamond (**Fig 1, right**) and the thermal equation of state reported by Anderson et al. [**10**] or a ruby sphere that was loaded with the sample on the side of the sample chamber. Sample properties were determined in the centre of the cell to limit peak overlaps with those of the pressure standards and to facilitate the diffraction pattern analysis using Rietveld methods. In total 650 diffraction data points were acquired that allowed monitoring the progression of the fcc-hcp transition in xenon and the effect of temperature on the later. The diffraction images were analysed using Rietveld refinement methods and the software package MAUD using our previous protocols [**4**, **5**, **6**].

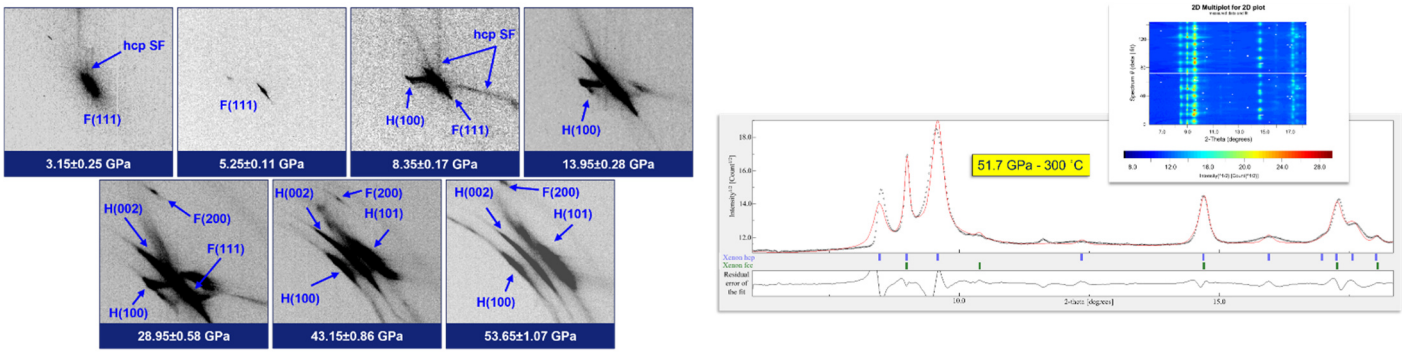

Fig. 2. Left panel*: Raw diffraction data acquired on pure xenon at 450 °C and up to 53(1) GPa.* ***Right panel****: integrated diffraction images analysed with the software package MAUD.*

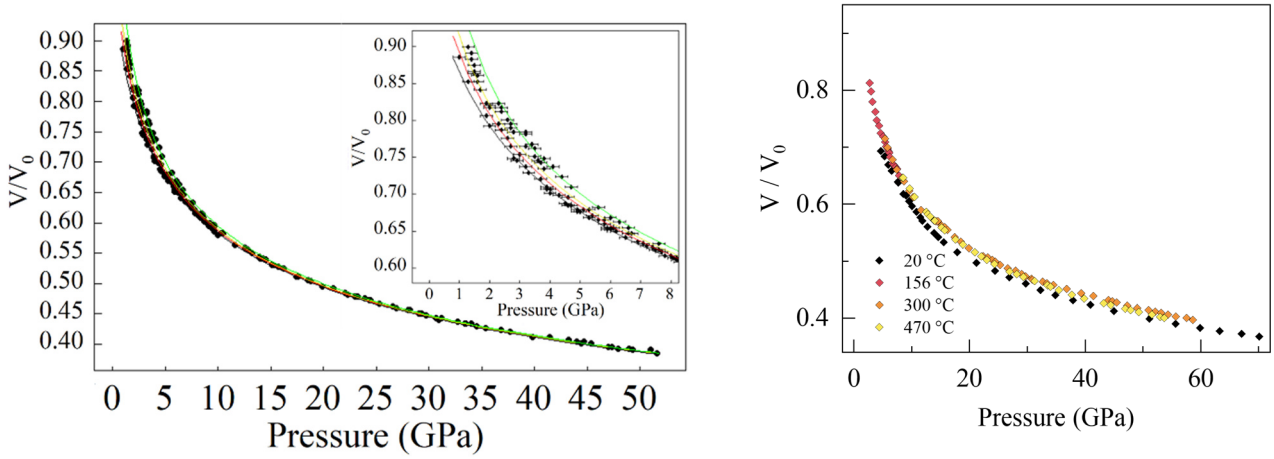

Fig. 3. Left panel: *Pressure evolution of the reduce crystallographic volume of fcc xenon along the three isotherms and fits to the data using a Birch-Murnaghan Mie-Grueneisen EOS formalism.* ***Left panel****: Pressure evolution of the reduced volumes of hcp xenon along the three isotherms.*

At present, the diffraction data have been analysed. The pressure evolution of the hcp xenon volume fraction together with the atomic volumes and the crystal domain sizes of the fcc and hcp phases have been extracted. The latter have been fitted to thermal equation of state formalisms to extract the thermoelastic data of xenon. We notice important anomalies in the compression behaviour that maybe related to the fcc-hcp transition and the transformational stresses that emerge in the host and daughter phases because of this transition. The anomalies are the lowest for the run conducted at the highest temperature. This suggests that elevated temperatures are needed to study the compression behaviour without artefacts due to the transition itself. Due to the limited amount of beamtime isothermal runs at higher temperatures and up to 1200 °C (temperature limited of the internally heated diamond anvil cell available at the ESRF sample environment) could not be performed. To complet this study in future we plan to submit a follow-up proposal.

BM23 experiment:

Complementary X-ray absorption spectroscopic (XAS) data of liquid and solid xenon were acquired at the beamline BM23 of the ESRF through inhouse research to achieve the aim of the proposal. The beamline optics comprised two Si(311) monochromator crystals in fixed-exit geometry coupled to two Pt-coated KB-mirrors employed for beam focusing and harmonic rejection. The X-ray beam was tuned over the xenon K-edge (34.6 keV) and was focused to 3*3 μm^2. The incident and transmitted beam intensities were measured using ionchambers mounted before and after the sample and filled with appropriate gas mixtures. The pressure was determined using a crystal of Sm:SrB_4O_7 loaded together with xenon in the sample chamber. The same RH-DAC was employed as for the ID15b run, except that only one DAC was employed equipped with nano-polycrystalline diamonds having a culet diameter of 600 µm were employed which are necessary to acquire glitch-free EXAFS data.

The aim of the XAS run was to study the solidification of xenon and the structural properties of the first-forming xenon crystal (***Fig. 4***). The latter was challenging to extract from the X-ray diffraction data due to significant peak breading (***Fig. 2 left panel***) potentially related to extensive thermal vibrations present in crystalline xenon at low pressure and high temperature.

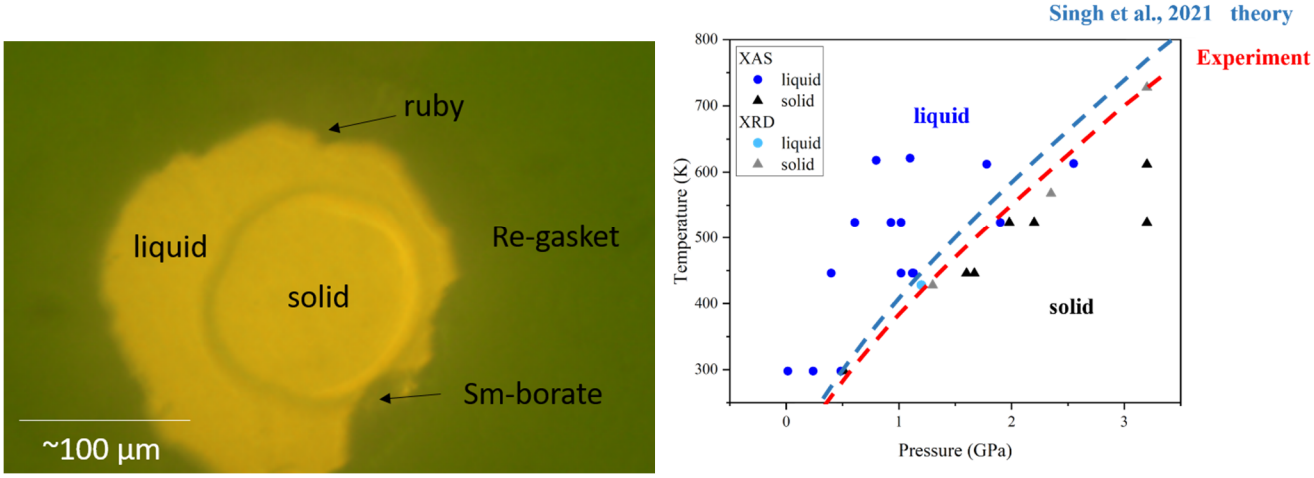

Fig. 4. Left panel: *View on the xenon sample during melting at 2.4 GPa and 640 K.* ***Right panel****: Probed P/T space of the XAS run.*

XAS data were analysed using the software package Athena and Arthemis. Solid and liquid xenon exhibit clear feature differences in the XANES region and could be therefore easily distinguished to establish the phase diagram shown in Fig. 4 (**right panel**). The extracted EXAFS data reveal however a very low amplitude of oscillations due to strong contributions of thermal vibrations at these low pressure but high temperature conditions. This small signal could only be resolved up to a k equal 5 $Å^{-1}$ with the photon flux provided at BM23 ($10^{\wedge 9}$ ph/sec after beam focalisation) despite its improvement by a factor of 3 thanks to the EBS. Such weak signals may be resolvable in future at ID24-DCM that provides 4 orders of magnitudes higher flux ($10^{\wedge 13}$ ph/sec) or at low temperature but high pressure conditions.

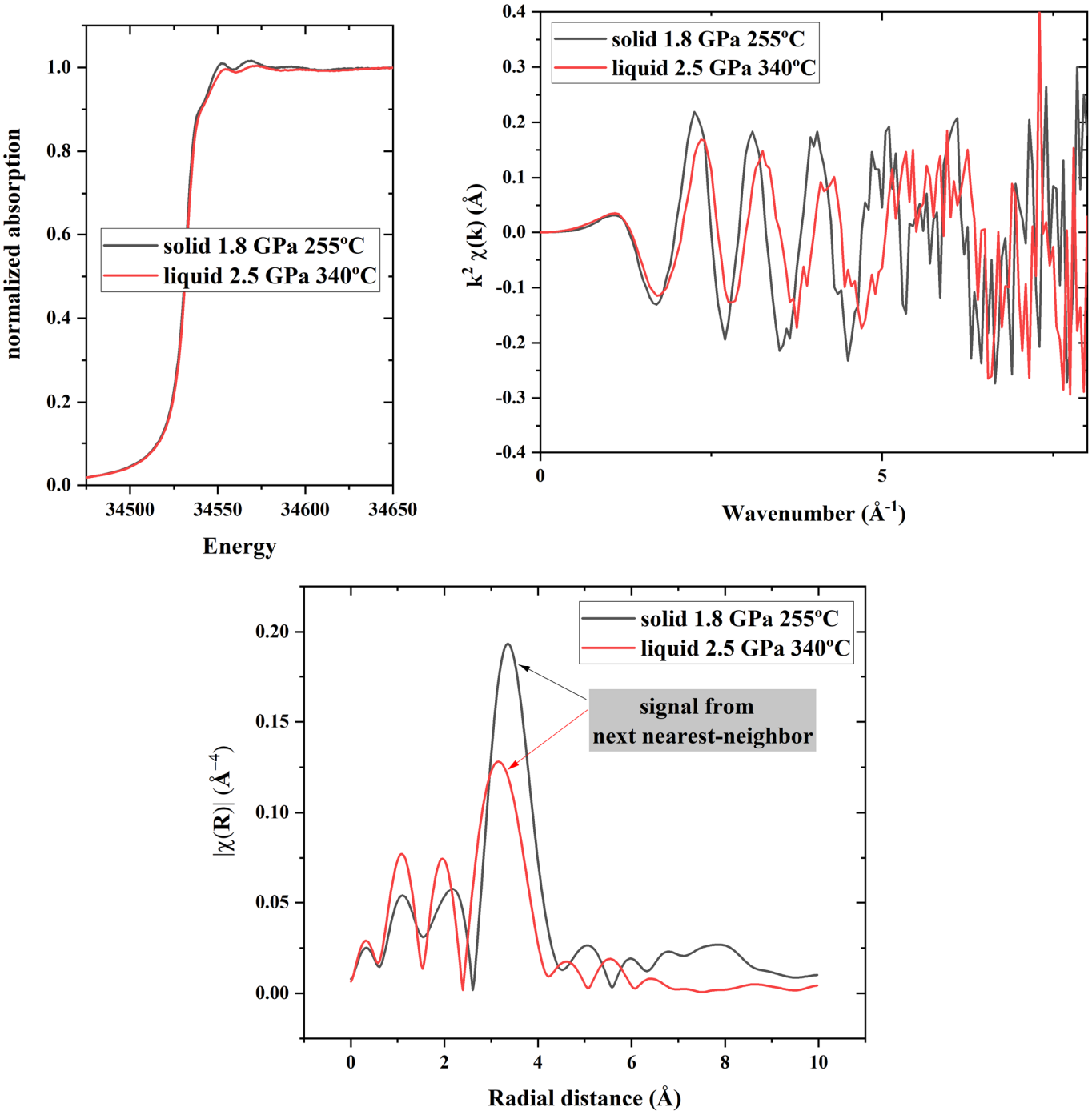

Fig. 5. Extracted XAS data of solid and liquid Xe at high pressure and temperature. **Top left panel:** XANES data**. Top right panel:** extracted EXAFS oscillations. **Bottom panel**: Magnitude of the Fourier transform.

XAS data analysis is ongoing while XRD data analysis has been finalized. The data and results currently prepared for publication. The new data will improve significantly our understanding of the physical properties of noble gas solids at non-ambient conditions and the effect of temperature on the progression of the fcc-hcp transition.

References

[1] Z. Nishiyama, Martensitic Transformation (Academic Press, New York, 1978). [2] H. Cynn, *et al.,* Phys. Rev. Lett. 86, 4552 (2001). [3] A. Di Cicco, *et al.,* Phys. Rev. B 54, 9086 (1996). [4] A.D. Rosa, *et al*., Phys. Rev. B 97, 094115 (2018). [5] A.D. Rosa, *et al*., Phys. Rev. B, in press, 2022 [6] A. Dewaele, *et al*. Phys. Rev. B 86, 014103 (2012). [7] D. Errandonea, *et al*.,, Phys. Rev. B 65, 214110 (2002). [8] A. Jephcoat, Nature 393, 355 (1998). [9] A.D. Rosa *et al.,* Earth Plant. Sc. Lett., 535, 116032 (2020). [10] Anderson et al., Journal of Applied Physics 65, 1534 (1989).