



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.

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Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

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.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- ☐ fill in a separate form for each project or series of measurements.
- ☐ type your report, in English.
- ☐ include the reference number of the proposal 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: X-ray diffraction on fluid nitrogen above 1 Mbar: Melting line and molecular to polymeric fluid transition.	Experiment number: HC 2490
Beamline: ID27	Date of experiment: From: 30/03/2016 to 03/04/2016	Date of report: 20/09/2017
Shifts: 18	Local contact(s): G. Garbarino	Received at ESRF:
Names and affiliations of applicants (* indicates experimentalists): Gunnar Weck* Frederic Datchi* Sandra Ninet* Jean Antoine Queyroux*		

Report:

Nitrogen possesses one of the strongest and most stable chemical bond in nature. This stability persists up to at least 110 GPa in the solid phase. Under further compression, the solid transform into a semiconducting amorphous phase above 150 GPa [1] at room temperature and to an extended covalent solid above 110 GPa under laser heating [2]. In the fluid, recent ab-initio simulations have predicted a transition toward a polymeric phase [3,4]. This transition is predicted to occur above the melting line at 90 GPa and 1700 K, is expected to be first order and is associated to a maximum of melting temperature. Three laser heating experiments performed in a diamond anvil cell (DAC) and using optical (speckle) [4] or Raman [5,6] measurements have probed the properties of nitrogen under high P-T conditions. They also found a maximum on the melting curve yet they disagree on its location (50 GPa for Ref[4], and 70 GPa for Ref[5,6]). Moreover, none of these experiments obtained evidence of polymeric nitrogen in the fluid. The goal of our experiment was to determine the nitrogen melting curve by X-ray diffraction and to measure its liquid structure factor up to above 1 Mbar in order to determine if the molecular fluid transforms into a polymeric liquid.

Experimental method

Five membrane diamond anvil cells were equipped with diamond anvils with culet sizes ranging from 300 μ m to 100 μ m. The samples were prepared to perform laser heating measurements. Since nitrogen is optically transparent in the infrared an absorbing material was needed to heat the sample. We have hence developed complex sample geometry with two boron doped diamond (C:B) plates defining a capsule which confines the volume of nitrogen probed by the X-ray beam. Blind rectangular slits are machined at the center of the C:B plates to allow space for the nitrogen sample. Each plate is deposited in a pit, realized by Focussed Ion Beam, at the center of the culet of the diamond anvils to ensure a good and steady positioning of the disks and the diamonds are coated with a thin layer Al₂O₃ or LiF for thermal insulation. The samples were laser heated by two YLF lasers entering the DAC from both sides in order to reduce axial temperature gradients. The temperature was measured using the thermal radiation collected at the center of the C:B plate.

X-ray diffraction measurements were performed at 33 keV with a Mar Image Plate detector. Finally, we have also used a multichannel collimator device to extract the very weak liquid sample signal from the background contribution due to the anvils. The usefulness of the MCC for liquid structure measurements in a DAC was recently demonstrated for hydrogen[7] and CO₂[8]. A total of 24 melting points were measured in between 40 and 125 GPa, with excellent reproducibility over the 5 experiments (see figure 1). The melting criterion was the appearance (respectively, disappearance) during temperature increase (decrease) of a diffuse scattering ring in the x-ray pattern coming from the liquid part of the sample. Our measurements show a monotonic increase of the melting temperature with pressure up to 116 GPa. Above 116 GPa, we observe a stiff increase in the slope of the melting curve when the sample crystallizes in the cg-N phase. These results thus contradict the theoretical predictions of a melting maximum at 88 GPa and 1700 K. We have also measured the evolution of the liquid structure factor ($S(Q)$) of nitrogen along the melting line up to 120 GPa. At low pressure, the nitrogen $S(Q)$ is composed of a main peak followed by weak oscillations as expected for a simple diatomic liquid. Going up in pressure the main peak position shift toward larger Q -values but the shape of the $S(Q)$ does not change and we do not observe the calculated strong structural changes predicted in the ab-initio simulations at the transition toward the polymeric liquid. In conclusion, our measurements invalidate the presence of a maximum melting temperature and indicate that fluid nitrogen remains molecular up to 120 GPa and 2400 K at odds with the most recent theoretical predictions of a first order phase transition between a molecular fluid and a polymeric liquid. These results have been recently submitted to Physical Review Letters.

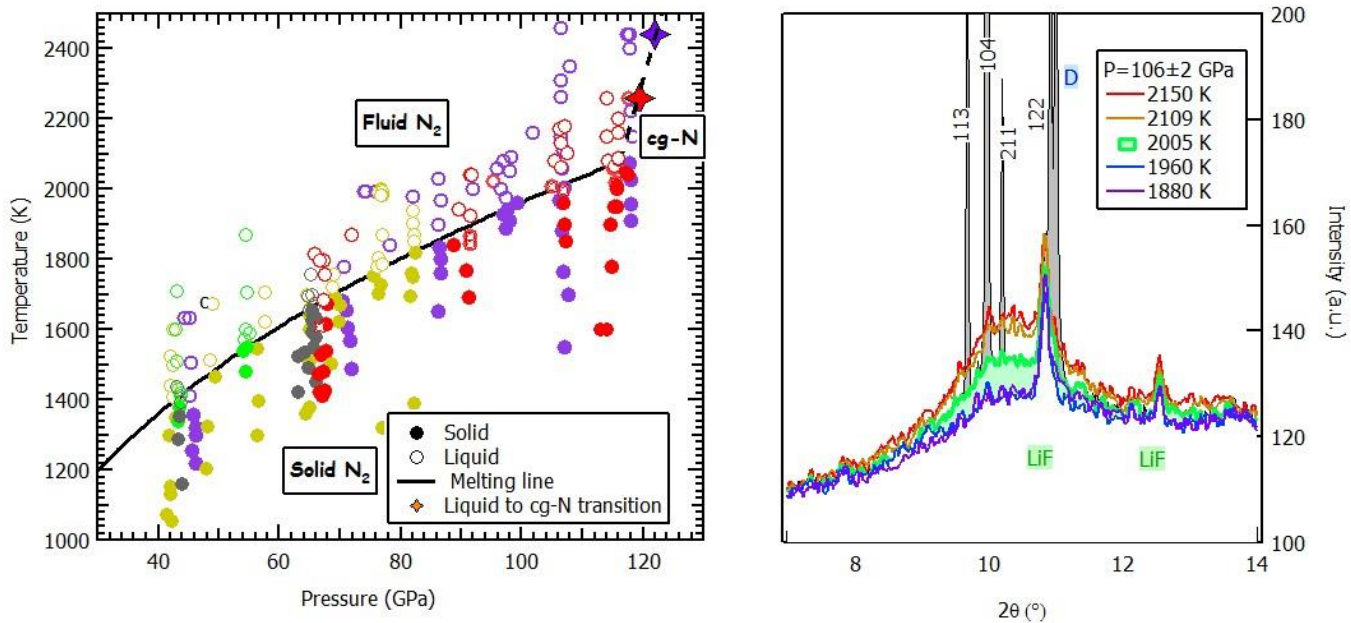


Figure 1: Determination of the nitrogen melting curve from 5 experiments (left) Pressure-Temperature conditions at which X-ray diffraction patterns have been collected. Each color represents a different sample. Solid (empty) circles represent the solid (liquid) phase. Lozenges indicate to P-T conditions at which the cg-N melting is crossed during pressure increase. (right) x-ray diffraction patterns collected at several temperatures around melting at 106 GPa. Solid nitrogen, diamond and LiF diffraction peaks are labeled. The broad diffuse ring centered at $2\theta=10.5^\circ$ at 2005 K and above comes from melted nitrogen.

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