EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF	**Experiment title:** High Pressure Symmetrisation of the H-bond in Ice: Phonon Dynamics	**Experiment number**: HC-5350
Beamline: ID28	**Date of experiment**: from: 03-May-2023 to: 09-May-2023	**Date of report**: 06-Sept-2023
Shifts: 18	**Local contact(s)**: Luigi Paolasini	*Received at ESRF:* 06-Sept-2023

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Report:

The purpose of the proposal was to investigate the high pressure phonon dynamics in ice over the entire first Brillouin zone, through the high-resolution inelastic X-ray scattering (IXS) technique. While literature investigations of this sort were limited so far to below 1 GPa, we aimed to push the high pressure IXS study of ice to pressures of several tens of GPa, at room temperature, aiming to unveil the unique dynamics related to the hydrogen bond symmetrisation occurring at the phase boundary between dynamically, proton disordered ice VII' and non-molecular ice X. Indeed, in principle, IXS is the proper probe to dig into the relevant subtle and crucial dynamical properties of this transformation, particularly the acoustic phonons, at a length scale comparable to the typical intermolecular distances.

We loaded 4 diamond anvil cells (DACs), 1 from our laboratories (DAC name: Re3), and 2 from ESRF (DAC names: Mbar2 and Mbar5). One out of the three DACs (Mbar2) was used as backup samples. All the DACs were loaded and tested in our laboratories prior the actual ESRF experiment. Particularly, we prepared fine powder ice VII samples by low temperature rapid compressions to 2-3 GPa in DACs and confirmed, through our laboratory XRD set-up, that the powders were actually vey fine an randomly oriented. As the gasket material we used Rhenium, and pressures were measured by the ruby fluorescence technique. The initial sample thickness and diameter (with reference to the gasket hole at room pressure) were equal to 20-25 μm (close to 10 μm at 50 GPa) and ≈ 50-100 μm, respectively. For the IXS, we used the (9,9,9) Si reflection configuration to have a good compromise between energy resolution (≈3 meV) and photon flux on the samples. The X-ray spot was focused down to 10 μm (FWHM, with gaussian spatial profile). Our previous experiences on fluid, low-Z samples in DACs, including water whose IXS was measured on the same beamline in the GPa pressure range [1-4] indicate that the present proposal was expected to be very challenging but feasible, in principle. Indeed, due to the much more extreme pressure conditions, sample thicknesses here were significantly smaller than those of the previously investigated samples [1-4] by up to a factor of 5-6, at tens of GPa. For each pressure point, the measurement of IXS over up to 18-20 distinct momentum transfer values required tipically 24 hours.

The IXS spectra exhibited very weak and poorely resolved inelastic peaks beyond the elastic line. We performed a preliminary fit of these spectra to a DHO model, convoluted to the instrumental spectral line-shape and taken together with a single analytical line for the elastic signal, for evaluating the E-Q dispersion curves reported in figure 1, at pressures of 3.7 GPa, 14.4 GPa, 16.7 GPa, 31.1 GPa, and 52.9 GPa. We identified three distinct modes labeled by black, green and red points in order of decreasing energy. Clearly, our dispersion curves depend very little on pressure despite the wide pressure range here investigated, in contrast with the literature acoustic dispersion curve for ice VII and Rhenium, the only materials involved here. Even more strikingly, the IXS spectra and, as a consequence, the dispersion curves, resulted to agree each others when spatially sampled throug the entire size (250-300 μm) of the culet. Particularly, those measured within the sample area are consistent with those measured on the gasket, although the X-ray spot was sufficinelty small to be able to definitely discriminate between the sample and the gasket. After the beam-time, we also measured the IXS spectra of a Rhenium foil at ambient conditions and found them to show an entirely negligible inelastic signal beyon the elastic line. Putting all these findings together led us to preliminarly conclude that our IXS spectra were entirely dominated by defects of some sort, likely related to the poorely compressible diamond anvils, which entirely overwhelmed the true inelastic signal of ice VII. More tests are needed in the future to consolidate these conclusions.

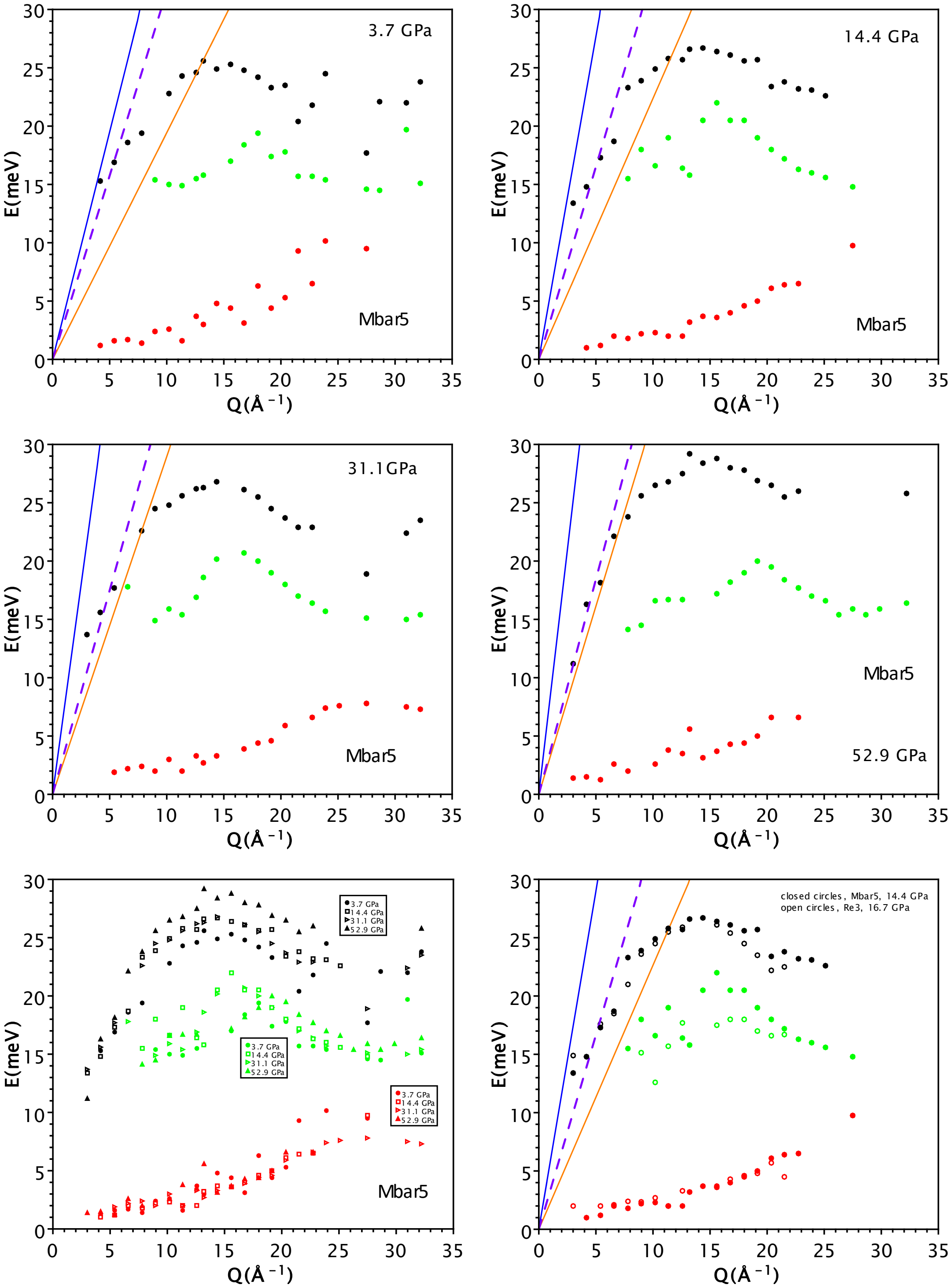

Figure 1: Top and middle panels: energy vs. exchanged momentum plots for sample Mbar5, at the four measured pressures: 3.7 GPa, 14.4 GPa, 31.1 GPa, and 52.9 GPa. Bottom left: superimposed E vs. Q plots for sample Mbar5, at the four measured pressures. Bottom right: superimposed E vs. Q plots for sample Mbar5 (closed circles) and Re3 (open circles) at two close pressures: 14.4 GPa and 16.7 GPa for Mbar5 and Re3, respectively. Blue line: extended acoustic, longitudinal dispersion curve for ice VII; violet, dased line: estimation for the extended acoustic limit of the present dispersion data (black points); brown line: extended acoustic, longitudinal dispersion curve for Rhenium.

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