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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.

ESRF	Experiment title: Lattice dynamics of MgSiO3 perovskite at high pressure: Theoretical and experiment	Experiment number: ES-403
Beamline: ID28	Date of experiment: from: 15/6/2016 to: 21/6/2016	Date of report: 13/09/16
Shifts: 18	Local contact(s): NGUYEN Thanh Tra	*Received at ESRF:*

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Report:

Bridgmanite ($MgSiO_3$-perovskite) is the main component of the Earth's lower mantle, and thus it's a key mineral for the interpretation of mantle geophysics. The interpretation of the seismic data (one-dimensional profile as well as tomographic data) in terms of chemical composition, mineralogy and temperature requires the knowledge of the elastic behavior of the deep Earth minerals at relevant pressure and temperature conditions. A wealth of theoretical lattice dynamical studies under ambient and high-pressure conditions has been carried out on $MgSiO_3$ perovskite [1,2], but only very recently the phonon dispersion relations have been experimentally measured under ambient condition [3; experimental report HS-4807]. The difficulty to synthesize crystalline samples of pure $MgSiO_3$-perovskite of good quality and of suitable size remains the main difficult to perform inelastic X-ray scattering (IXS) experiments on this important mineral. In particular, prior to here-described measurements, the phonon dispersions under high pressure were still experimentally unexplored.

Experiment ES-403 is thus the follow up of the experiment HS-4807, where IXS measurements were carried out only at the ambient conditions. Bridgmanite crystals from the same batch previously used were selected and tested by Single Crystal X-Ray Diffraction. The highest quality crystals with the smallest size were further cut by a combination of ion slicing and FIB technique to obtain samples of dimensions, suitable for diamond anvil cell (DAC) experiments. SC-XRD tests were also carried out after the FIB cut to check the crystallinity and the rocking curve of samples (better than 0.2 degrees).

Three membrane-type DACs, equipped with Re gaskets and 300 μm culets diamonds, were loaded with so-prepared crystals, neon gas as pressure transmitting medium, and a ruby chip as pressure calibrant. Pressure was increased up to ~8 GPa and samples checked by diffraction in order to define the orientation matrix and to select those with the most favorable orientation.

First principle calculations were performed before the experiment, within the generalized gradient approximation to the density functional theory in Perdew-Burke-Ernzerhof parameterization as implemented in the CASTEP code [4]. Results for P = 0 GPa, P=30GPa and P= 60GPa were used as guideline for the IXS experiment.

We performed IXS measurements on sample Xst3b, with lattice constants a(Å): 4.9292(6), b(Å): 6.9008(9) and c(Å) 4.7815(7), V(Å^3): 162.64(6) and density: 4.107 gm/cm^3, and size around 60x30x25 μm, and on sample P11, with lattice constants a(Å): 4.9178(9), b(Å): 6.887(3) and c(Å) 4.761(2), V(Å3): 161.3(3) and size around 50x30x30 μm.

The instrument was operated using the Si (9 9 9) configuration, with incident photon energy of 17.794 keV and a total instrumental energy resolution of 3 meV full-width-half-maximum (FWHM). The Si

(9,9,9) configuration has been proven to get enough flux to collect good-quality data in reasonable amount of time (~60-90s per point for lower q, ~150-210s per point for higher q). The dimensions of the focused x-ray beam were 25×60 μm^2 (horizontal×vertical, FWHM), further reduced by slits to 25×40 μm^2. The momentum resolution was set to 0.3 nm^{-1}.

The energy position was extracted by fitting a Lorentzian model function, convoluted with an experimentally determined energy resolution, utilizing a standard $\chi 2$ minimization.

-Experiments at P = 8 GPa:

Sample Xst3b was of very good crystalline quality, but oriented in (121) direction after the loading into the DAC. As this is not a principal direction, we only performed test measurements of longitudinal and transverse acoustic modes along the available directions.

Sample P11 was more favorably oriented, in the (100) plane after the loading into the DAC, and we could measure inelastic spectra starting from several strong reflections along the b* and c* directions.

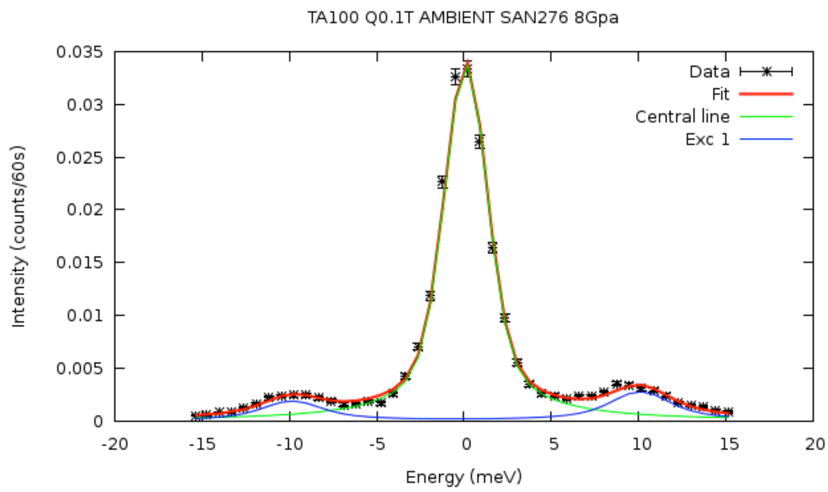

Figure 1: Example of collected IXS spectra. TA (100) $_{<010>}$ at reduced q=0.1 measured at 8 GPa. Red lines are fits to the experimental points.

Specifically, we probed the TA (100) $_{<010>}$, TA (001) $_{<010>}$, LA (010), LA (101), and TA (010) $_{<101>}$ phonons (see Figure 1). Detailed data analysis is still in progress.

-Experiment at P = 25 GPa:

A second set of IXS measurements was carried out on sample P11 at 25 GPa, to follow the evolution of the longitudinal and transverse acoustic modes with increasing pressure. The sample developed a twinning that limited the accessible directions to measure inelastic spectra, and rocking widths deteriorate to 0.3-0.4 degrees. Nevertheless, we were able to measure TA (100) $_{<010>}$, TA (001) $_{<010>}$, LA (001), and TA (101) $_{<010>}$ phonons at this pressure (see Figure 2).

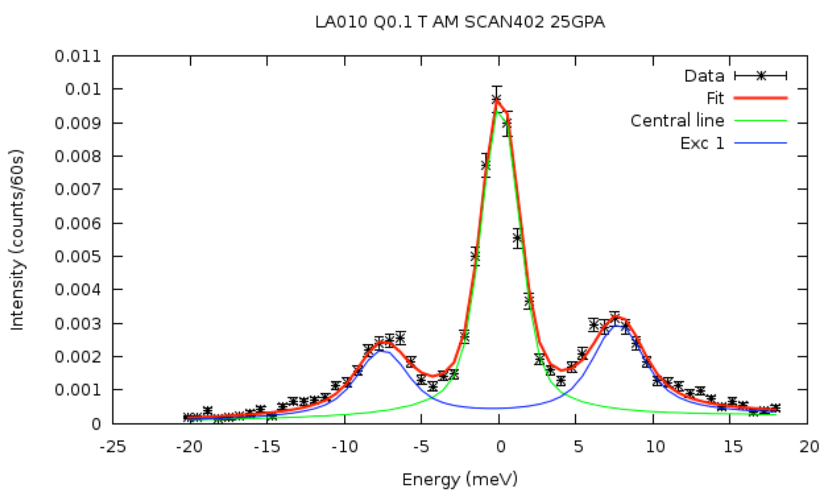

Figure 2: Example of collected IXS spectra. LA (0,1,0) phonon at reduced q=0.1 measured at 25 GPa. Red lines are fits to the experimental points.

After the experiments both samples were recovered. Sample P11 is still crystalline as shown by SC-XRD performed on the recovered sample.

In summary, we successfully performed inelastic scattering measurements of bridgmanite at 8 and 25 GPa, so to follow the variation of the phonon energies with increasing pressure. Although a pressure of 25 GPa correspond to the upper part of the lower mantle, more experiments are needed to investigate the lattice dynamics of this phase down to lower mantle conditions. Experiment ES-403 clearly demonstrates the feasibility of such a project, provided working with thinner samples. Our goal is to combine experimental IXS study with parameter-free model calculations to provide the complete lattice dynamics description of geophysical relevant materials, as illustrated here for the case of $MgSiO_3$ bridgmanite, without the need to individually record all the phonon branches along all the high symmetry directions.

References

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[4]Clark, S., M. Segall, C. Pickard, P. Hasnip, M. Probert, K. Refson, and M. Payne, First principles methods using CASTEP, Z. Kristallogr. *220*, 567–570 (2005)