ESRF	Experiment title: Lattice dynamics of MgSiO3 perovskite at high pressure: Theoretical and experiment	Experiment number: HS-4807
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Shifts: 18	Local contact(s): Michael Krisch	*Received at ESRF:*

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Report:

The Earth's lower mantle is considered to consist principally (70–80 wt.%) of $MgSiO_3$ perovskite (bridgmanite). 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 [1].
Because of its geochemical and geophysical importance, the physical and thermodynamic properties of $MgSiO_3$ perovskite have been extensively studied experimentally and theoretically. However, in spite of a number of theoretical lattice dynamical studies have been reported [2,3], so far no experimental determination of phonon dispersion relations have been possible due to the difficulties to synthesize single-crystalline samples of suitable quality and dimensions.
During the experiment HS-4807 we started a combined experimental and theoretical project aiming at the investigation of the lattice dynamics of $MgSiO_3$ at lower mantle conditions. Our intention is to follow the same approach carried out for MgO [4].

-Experiment at ambient conditions:

$MgSiO_3$ single-crystals have been synthesized in a multi-anvil press in Sendai (Japan) and, after SCXRD tests, best crystals were selectd. $MgSiO_3$ perovskite has an orthorhombic symmetry (sp. gr. *Pnma*), the crystal used for the experiment has lattice constants: *a*(Å): 4.9436(3), *b*(Å): 6.9149(8) and *c*(Å) 4.7902(6), V(Å^3): 164.75(3) and density: 4.107 gm/cm^3, and an average size around 50x50x100 microns.
The single-crystal was oriented and polished to obtain a perpendicular scattering surface.
We measured inelastic spectra along several high-symmetry directions, starting from different strong reflections along the a* and b* directions. 148 inelastic spectra were measured. Representative IXS spectra along different directions in reciprocal space at selected reduced momentum transfers are reported in figure 1. The spectra are characterized by an elastic line, centered at zero energy transfer, and several inelastic features in the energy range between 20 and 110 meV, corresponding to acoustic and optical phonons. A logarithmic intensity-scale is chosen for better visualization of the high-energy phonon modes, which have a much weaker intensity.

First principle calculations were performed within the generalized gradient approximation to the density functional theory in Perdew-Burke-Ernzerhof parameterisation as implemented in the CASTEP code [5]. The results of the theoretical calculations, which account for the inelastic contribution, are represented by solid blue lines in the individual panels.

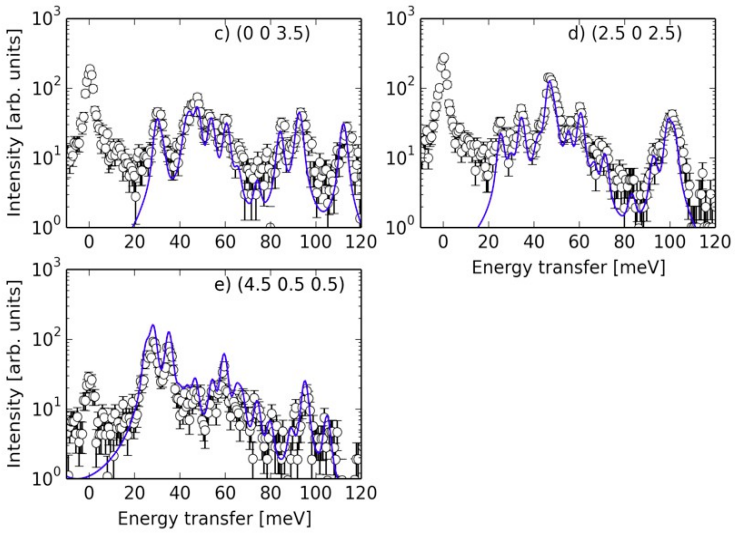

Figure 1. Experimental (open symbols with their corresponding error bars) and calculated (blue lines) IXS spectra of single crystal $MgSiO_3$ at selected reciprocal space point (a) X, b) Y, c) Z d) U and e) R point). The *ab initio* calculated intensities were convoluted with the experimental resolution function and the calculated energy transfer scaled by 1.05

Experimental and theoretical IXS intensity maps along three selected principal directions in reciprocal space are compared in Fig. 2. Besides a strong contribution from the elastic line close to the (0 4 0) point and some artifacts due to the interpolation routine used for the reconstruction of the IXS maps from individual fixed-q IXS experimental spectra, we note a very good agreement in terms of phonon energies and intensities. Together with the results displayed in Fig. 1 this proves that our calculations not only correctly predict the phonon energies (after a modest overall scaling), but also the phonon eigenvectors, which govern the phonon intensities [6].

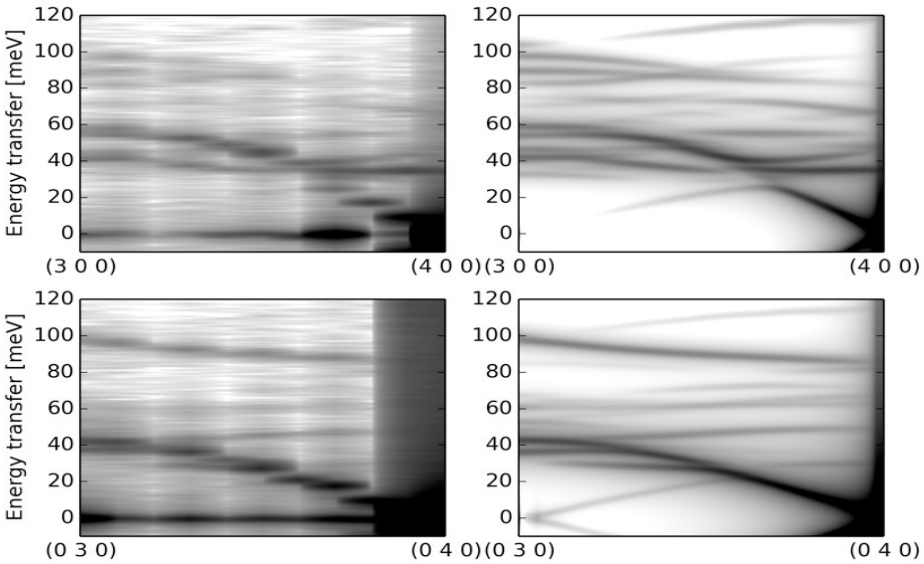

Figure 2. Experimental (left) and calculated (right) IXS intensity maps along the indicated directions on a logarithmic intensity scale. The experimental maps consist each of eleven spectra linearly interpolated to 200 q-points. The calculated intensities are convoluted with the experimental resolution function and the energy transfer is scaled by 1.05.

The $MgSiO_3$ phonon dispersion along selected high symmetry directions is reported in Fig. 3, For the low-energy part we present the experimentally determined phonon energies. The agreement to the calculation is excellent. Inspection of the complete phonon dispersion - which extends up to 120 eV - reveals that the correct assignment of an experimentally observed phonon mode becomes increasingly more difficult due to the high density of phonon branches. On the other hand, the excellent agreement between experiment and

theory (after a simple rescaling) as witnessed in Figures 1 – 3 allows assuming that our calculation correctly describes the lattice dynamics of $MgSiO_3$. The phonon dispersion of the optical branches is rather complex and shows pronounced splitting of longitudinal optical and transvers optical branches. The splitting is due to large Born effective charges. We calculated the Raman active modes energies and a very good agreement arise when compared to experimental values [7].

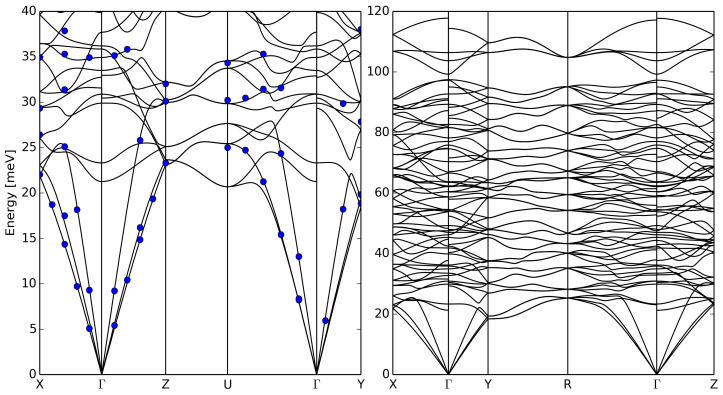

Figure 3. Calculated phonon dispersion relations (solid lines) along selected high symmetry directions for the low energy part (left) and the full energy range (right). Experimentally determined phonon energies are plotted as blue dots, the calculated energies are scaled by 1.05.

The theoretical results were used to derive the partial and total phonon density-of-states (DOS), that allows the derivation of important thermodynamic properties total energy E and free energy F; Entropy S and heat capacity C_v [Wehinger et al., submitted].

Our experimental study combined with parameter-free model calculations can provide the complete lattice dynamics description of geophysically relevant materials as illustrated here for the case of $MgSiO_3$ bridgmanite without the need to record the phonon branches one-by-one along all the high symmetry directions. We are now planning to extend this approach at high pressure.

References

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