ESRF	**Experiment title:** Investigation of the solid state amorphization transition in Stishovite by inelastic X-ray scattering	**Experiment number**: HS 3302
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Report:

In the present work we demonstrate that IXS powder measurements in combination with quantum mechanical calculations can provide the complete description of lattice dynamics (LD) by investigating the stishovite, a high pressure SiO_2 polymorph [*Bosak et al.*, 2009]. Stishovite has been chosen as a benchmark case, since (i) its geophysical relevance is currently discussed in relation to the seismic signature of the X-discontinuity at a depth about 300 km [*Williams et al.*, 2005] and hence we anticipate a renewed discussion of its thermodynamic properties, and (ii) there is no complete experimental data set for its LD.

The polycrystalline stishovite was synthesized from amorphous SiO_2 at 12 GPa and 1200°C, using the USSA-2000 high-pressure apparatus at the Mineral Physics Institute, Stony Brook University. No preferred orientation was revealed by x-ray diffraction. The single crystal of $0.1\times0.15\times0.25$ mm^3 size was grown hydrothermally in the system SiO_2-H_2O. The instrument was operated at 15816 eV and 17794 eV, providing an energy resolution of 6.0 meV and 3.0 meV full-width-half-maximum (FWHM), respectively. The single crystal measurements below 20 meV and polycrystalline measurements were performed with 3 meV resolution. Phonons of the single crystal with energies above 20 meV were explored with 6 meV resolution.

Representative experimental data obtained from the powder measurements are shown in Fig. 1 in comparison to the DFT-predicted values. An outstanding agreement between the datasets is achieved by applying a scaling factor 1.05 to the calculated phonon energies. The necessity of scaling was expected, as DFT-GGA calculations generally give too low phonon frequencies. The major deviations are observed below 20 meV and are fully explained by the contribution of elastic scattering due to the grain boundaries and the proximity of Debye-Scherrer rings. No multiphonon contributions have been taken into account.

The agreement between the experimental and rescaled theoretical data is retained in the whole accessible *Q*-range. Thus, the validity of the model is proven for *any* crystallographic direction, as orientation averaging probes the low-symmetry directions as well. Relative intensities of phonons are naturally embedded in the experimental spectra thus providing the instrument to check the consistency of the phonon eigenvectors within the model. The phonon dispersion for high symmetry directions appears as a by-product. As a decisive test, we have confronted the polycrystalline results with data obtained from a single crystal in the "conventional fashion". Fig. 2 displays the phonon dispersions along the three main high-symmetry directions. Excellent agreement between the experimental and calculated dispersion is restored after the theoretical phonon energies scaling by the same factor of 1.05, established from the polycrystalline experiment.

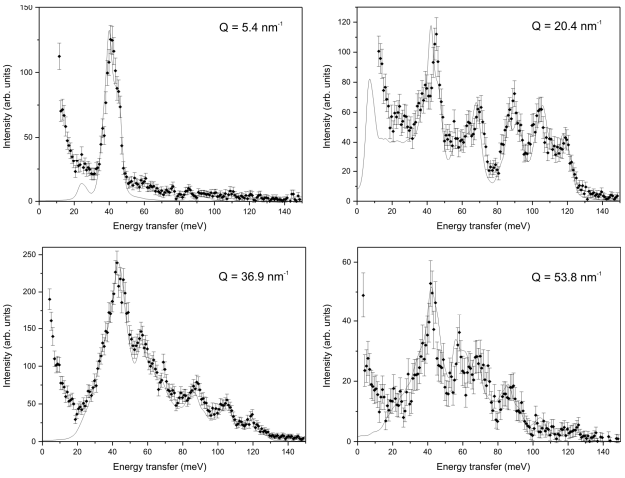

FIG. 1. Representative polycrystalline IXS spectra of stishovite recorded at: Q = 5.4 nm^{-1}, 20.4 nm^{-1}, 36.9 nm^{-1}, and 53.8 nm^{-1} (circles with error bars) compared to *ab initio* calculations (solid lines). A scale factor of 1.05 has been applied to the energies obtained by DFT-GGA calculations.

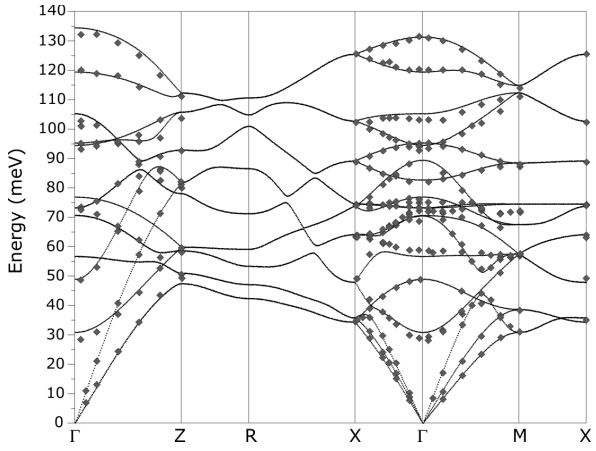

FIG. 2. a) Dispersion relations for stishovite along high symmetry directions. Single crystal IXS data (points) are compared to *ab initio* calculations (lines). A scaling factor of 1.05 is applied to the calculated energy scale.

Once the (rescaled) LD model is validated, it provides immediately the VDOS. Derived temperature dependences of such macroscopic parameters as specific heat, entropy, and Helmholtz free energy agree very well with available experimental data. The elastic moduli derived from the DFT-GGA calculation by the stress-strain method [*Winkler et al.*, 2001] and properly rescaled are in excellent agreement with those obtained experimentally from Brillouin light scattering (BLS) [*Weidner et al.*, 1982, *Brazhkin et al.*, 2005, *Jiang et al.*, 2009]. A significant deviation (~20%) remains for C_{12}, while all other moduli and the integral properties (bulk modulus and Debye velocity) converge very well, thus confirming the predictive power of DFT-GGA stress-strain calculations.

Bosak, A., I. Fischer, M. Krisch, V. Brazhkin, T. Dyuzheva, B. Winkler, D. Wilson, D. Weidner, K. Refson, V. Milman (2009), *Geophys. Res. Lett.*, in press

Williams, Q., and J. Revenaugh (2005), *Geology*, *33*, 1-4.

Winkler, B., M. Hytha, M.C. Warren, V. Milman, J.D. Gale, J. Schreuer (2001), *Zeitschrift für Kristallographie*, *216*, 67-70.

Weidner, D.J., J.D. Bass, A.E. Ringwood, and W. Sinclair (1982), *J. Geophys. Res.*, *87*, 4740-4746.

Brazhkin, V., L. McNeil, M. Grimsditch, N. Bendeliani, T. Dyuzheva, and L. Lityagina (2005), *J. Phys.: Condens. Matter*, **17**, 1869-1875.

Jiang, F., G.D. Gwanmesia, T.I. Dyuzheva, and T.S. Duffy (2009), *Physics of the Earth and Planetary Interiors*, *172*, 235-240.