Anharmonic lattice dynamics of Ag_2O studied by inelastic neutron scattering and first principles molecular dynamics simulations
Supplemental Material

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To separate the effects of quasiharmonicity and explicit anharmonicity, the mode frequency $\omega_j = \omega_j(V,T)$ is expressed as a function of volume and temperature

$$\left(\frac{\partial \ln \omega_j}{\partial T}\right)_P = -\gamma_j \beta + \left(\frac{\partial \ln \omega_j}{\partial T}\right)_V \quad (1)$$

where j is the phonon mode index, β is the volume thermal expansivity and γ_j is the mode Grüneisen parameter. The left-hand side is the temperature-dependent frequency shift at constant pressure, and includes contributions from both quasiharmonicity and explicit anharmonicity. The first term on the right-hand side, the isothermal frequency shift as a function of pressure, is the quasiharmonic contribution to the frequency shift. The second term on the right is the pure temperature contribution to the frequency shift from the explicit anharmonicity. From the difference of the isobaric and isothermal frequency shifts, the explicit anharmonicity can be determined.

In a molecular dynamics simulation, the quasiharmonic contribution can be evaluated explicitly by turning off the temperature-dependent anharmonicity. In principle, this method is equivalent to the QHA method implemented with self-consistent lattice dynamics,[?] and in practice we have found this to be true. For example, we performed simulations at 40 K for volumes characteristic of 400 K, which produced a pressure of 0.45 GPa. This calculation therefore removed the temperature effect while preserving the quasiharmonic volume effect at 400 K. The corresponding phonon DOS curves from MD calculations are shown in Fig. 1. By comparing the phonon spectrum of a simulation at 40 K and 0.45 GPa with a simulation at 400 K, the pure temperature dependence is identified. From the spectra of Fig. 1, it is found that the explicit anharmonicity dominates the softening and broadening of the phonon spectra. All features in the phonon spectra with the QHA showed little change with temperature, except for small stiffenings at high energies.

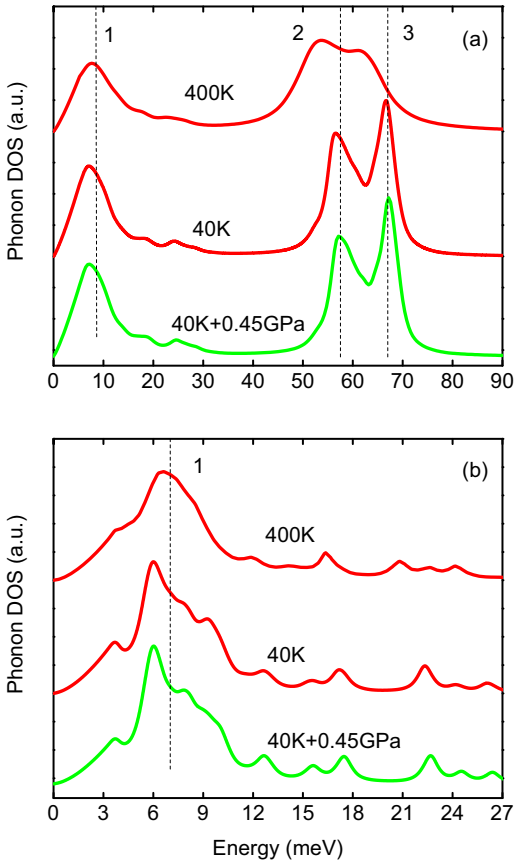

FIG. 1. Neutron weighted phonon DOS of Ag_2O with the cuprite structure from MD simulations. The green spectrum is the MD simulated phonon DOS at 40 K and 0.45 GPa. Vertical dashed lines are aligned to the major peak centers at 40 K and labeled by numbers. The incident energy was 100 meV for panel (a), and 30 meV for panel (b). The spectra were convoluted with the resolution function characteristic of ARCS for the different energies of the incident neutron beam.