Energy barriers for proton hopping

We calculate the energy barrier for a proton jump in the HOC-11 structure. We used the nudged elastic band (NEB) method. Because of the “ballistic” ordering, a single proton jump is not likely and proton jumps must be coordinated. For this reason we must consider a more orderly disorder. Dynamically, jumps could occur in sequence as a soliton propagation. The energy barrier decreases with pressure, thus there is a higher probability for proton disordering under compression. The energy for a single proton jump is in overall small, suggesting configuration coexistence (disorder). We further confirm that each layer (XY plane) should remain ordered, otherwise the backward barrier will vanish, and the “jumped” atomic configuration is not stable.

Order-disorder transition with mc-QHA

We attempt to reproduce the disordering transition in δ-OH using the 4 configurations proposed by Tsuchiya et al. (2). In the 0-10 GPa (300 K) range, the HOC-12 is the most important structure, but it becomes unstable at 10 GPa. In the 10-20 GPa range, the most important structure is HOC-11*.

Vibrational stability

Different supercell structures develop vibrational instabilities at different pressures: HOC-12, 10 GPa, HOC-11*, 20 GPa, HOC-12, 20 GPa. The softening of OH-stretching modes could indicate the beginning of proton tunneling. Different supercell structures develop vibrational instabilities at different pressures: HOC-12, 10 GPa, HOC-11*, 20 GPa, HOC-12, 20 GPa. The softening of OH-stretching modes could indicate the beginning of proton tunneling.

Anomalies in neutron diffraction

In the neutron diffraction experiment, the disappearance of [021] normalized by [110] peak indicate the change in space group, as a sign of entering a fully-disordered regime. This might not necessarily so. According to calculation, HOC-11* supercell does not have [021] peak. Its growing population accompanied by the disappearance of HOC-12 could also explain this result.

Pressure evolution of mode frequency for supercell structures at 1/3 point (zone center).

References


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Methods & calculation details

- Quantum ESPRESSO
- 4 x 4 x 4 point meshgrid
- GGA-PBE-EPAW [5]
- DFT Phonon at 2 x 2 x 2 point grid interpolated to an 8 x 8 x 8 grid
- Multiconfiguration-QHA [4]
- Climbing image NBO [10] used to calculate proton jump energy barrier.