Ab initio investigation of order-disorder transition in δ-AlOOH

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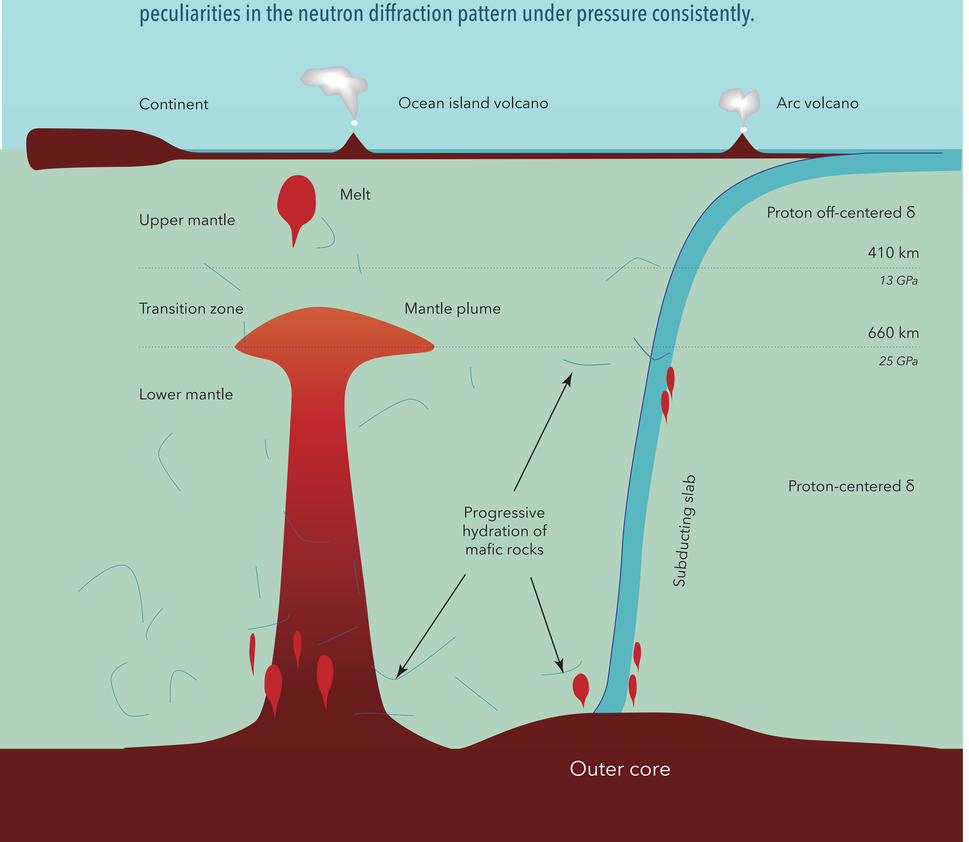
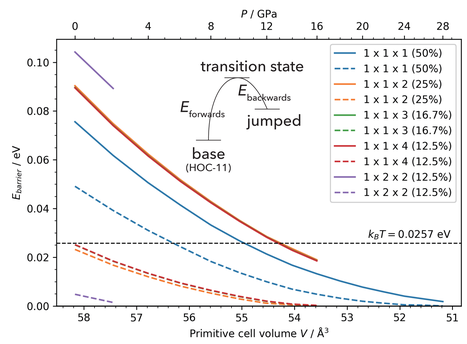
δ-AlOOH is a high-pressure polymorph of boehmite (α-AlOOH) with a wide pressure and temperature stability field. Previous mineral physics studies indicate that this mineral plays a vital role in the transport of water into Earth's deep interior, possibly down to the core-mantle boundary (CMB) at ~136 GPa. Attempts to resolve the structure of this mineral under pressure revealed that hydrogen bonds (H-bond) "symmetrize" under compression, a phenomenon similar to that observed in the ice VII- or ice VIII-X transition in H_2O. Like H_2O-ice, δ-AlOOH comes with its own "ice-disorder rules" and disorder is also observed experimentally prior to H-bond symmetrization [1]. H-bond disorder in δ-AlOOH had been suggested by an ab initio calculation as a possibility based on the intensities of Raman active OH-stretching modes [2].

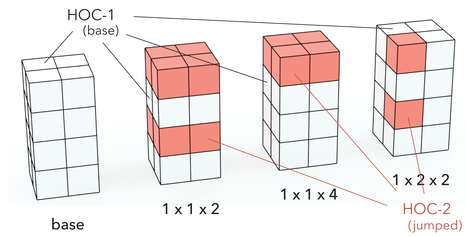
In this ab initio study, we address the order-disorder transition phenomenon that precedes H-bond symmetrization from several perspectives. We address: a) the accuracy of standard DFT functions to address the structural properties of this problem, b) energy barriers for proton-hopping, c) vibrational stability and the pressure-temperature range of validity of the quasiharmonic approximation (QHA), and d) order-disorder transition using a multi-configuration QHA calculation [3,4]. With these results, we can reproduce the structural behavior and some peculiarities in the neutron diffraction pattern under pressure consistently.



Energy barriers for proton hopping

We calculate the energy barrier for a proton jump in the HOC-11 structure. Wen used the nudged elastic band (NEB) method. Because of "ice-like" 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.

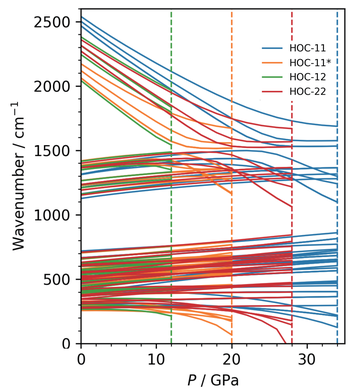




Top: the pressure dependence of energy barrier (dashed line and solid line denotes forward and backward jump, respectively) calculated with NEB. Bottom: assume one single jump cause a structure change from HOC-1 to HOC-2, the schematic plot for the base and jumped structure.

Vibrational stability

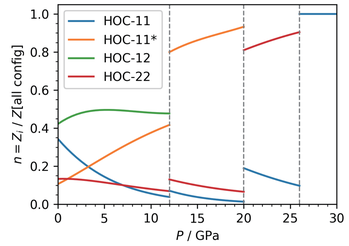
Different supercell structures develop vibrational instabilities at different pressures: HOC-12: 10 GPa, HOC-11*: 20 GPa, HOC-12: 20 GPa. The softening of OH-stretching modes could indicate the beginning of proton tunneling.



Pressure evolution of mode frequency for supercell structures as at Γ point (zone center).

Order-disorder transition with mc-QHA

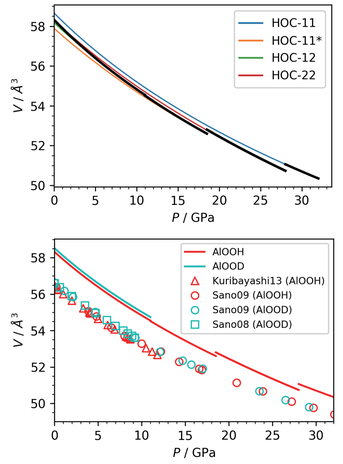
We attempt to reproduce the disordering transition in "δ" using the 4 configurations proposed by Tsuchiya et al. [2]. In the 0-10 GPa (300 K) range, the HOC-12 is the most important structure, but it becomes unstable at 10 GPa. In the 10-20 GPa, the most important structure is HOC-11*.



Pressure dependence at 300 K of configuration populations calculated with multiconfiguration QHA.

Equation of state at 300 K

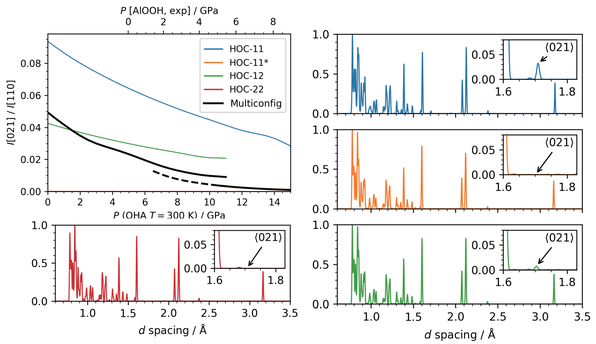
We are able to reproduce the equation of state (EoS) for δ at 300 K with mc-QHA. The overestimation of volume is caused by the usual DFT error but we are able to reproduce the overall compression change consistently.



Top: Compression curves for the 4 proton ordered supercells. Bottom: Compression curves for AlOOH and AlOOD at 300 K compared with experimental data [6-8].

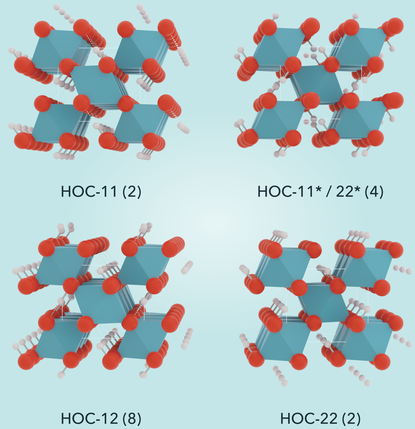
Anomalies in neutron diffraction

In the neutron diffraction experiment [1,6], the disappearance of <021> 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* supercells does not have "<021> peak". Its growing population accompanied by the disappearance of HOC-12 could also explain this result.



Diffraction intensities calculated with CrystalDiffract. Top left: the pressure evolution of [021] normalized by [110] peak. Other four: the diffraction pattern of HOC supercells.

Structures



(number in the parenthesis denotes multiplicity)

Methods & calculation details

- Quantum ESPRESSO
- 4 x 4 x 4 k-point meshgrid
- GGA-PBE-EPAW [5]
- DFPT Phonon at 2 x 2 x 2 q-point grid interpolated to an 8 × 8 × 8 grid
- Multiconfiguration-QHA [4]
- Climbing image NEB [9,10] used to calculate proton jump energy barrier.

References

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