Ab initio investigation of H-bond disordering in δ-AlOOH

δ-AlOOH is an important hydrous phase that carries water into lower mantle via slab subduction. H-bonds (O—H···O) in δ are asymmetric at lower pressure. They undergo symmetrization under compression and become degenerate ionic bonds (O—H—O) after the process. H-bonds in δ are localized and independent from the Al-O-Al network which determine the structure. δ is an ideal example to study disordering and tunneling, the two process usually associates with the symmetrization because of the reduced energy barrier that facilitates the redistribution of protons.

The H-bond disordering in δ was modeled with 1x1x2 supercells. Disordering is limited to 1D (z) and H-bond arrangements in (x,y) was restricted by "ice-rule"-like rules.

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Energy barrier

The energy barrier for a single proton jump from nudged-elastic band (NEB) calculation show barrier decreases vs. pressure before full symmetrization. Compared to k_BT [4] at 300 K, shows tunneling could take place at ~10 GPa, agrees with MD simulation by Bronstein et al. [5].

Experimental evidences related to the 300 K multistage transition: (a) IR peaks [1] (b) OH-bond lengths [2] (c) neutron diffraction 021 peak intensity [2] (d) compression curve [3]

H-bond disordering roughly estimated by comparing energy barrier to k_BT for ice [4].

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Phonon properties

- Two OH-stretching modes observed in MD at 0-10 GPa; one observed after 10 GPa. Disappearance of high-frequency mode corresponds to disappearance of H-aligned (HOC-11, 22) configuration.

Thermodynamic properties

We perform a multiconfiguration QHA to calculate thermodynamic properties of \( \delta \). The compression curve from mc-QHA shows that disordering explains well the greater compressibility at \( \sim 0-8 \) GPa.

\[
\begin{align*}
\rho_m(V, T) &= \frac{m}{Z_{\text{QHA}}} = \frac{g_m \exp\left(-\frac{F_m(V, T)}{kT}\right)}{\sum g_m \exp\left(-\frac{F_m(V, T)}{kT}\right)} \\
F_{\text{QHA}}(V, T) &= k_B T \ln Z_{\text{QHA}}(V, T)
\end{align*}
\]

(a) Pressure evolution of HOC-11, 11*, 12, and 22 population from mc-QHA at 300 K. (b) Comparison between HOC-11, 11*, 12, and 22 EoS and the multi-configuration overall EoS; (c) Comparison of \( \delta \)-AlOOH (red) and \( \delta \)-AlOOD (blue) at 300 K. Curve represent overall EoS from mc-QHA.

Neutron diffraction intensity & bond length

Phonon modes vs. pressure from supercell MD [1]. Two OH-stretching modes observed in MD at 0-10 GPa; one observed after 10 GPa. Disappearance of high-frequency mode corresponds to disappearance of H-aligned (HOC-11, 22) configuration.