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High-pressure proton disorder in brucite

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ABSTRACT

In this paper we explore the structure and physical properties of brucite over a wide range of pressures with density functional theory using the variable cell-shape plane wave pseudopotential method in the local density (LDA) and generalized gradient (GGA) approximations. We probe the energetics underlying the structure and dynamics of the proton sub-lattice by performing a series of constrained and unconstrained static calculations based on an energetically stable $\sqrt{3}\times\sqrt{3}\times1$ super-cell wherein proton locations are related to the 6*i* Wyckoff sites as opposed to the ideal 2*d* site. The displacement of the hydrogen atom from the threefold axis increases with increasing pressure. This means that even in the absence of thermal energy, the protons are frustrated and would be expected to exhibit long-range disorder akin to a spin glass. To shed light on the dynamic nature of the proton hopping between the 6*i*-like sites, we determined the activation energy barrier for such jumps. We found that the energy barrier increases with compression, possibly indicating a transition from dynamic proton disorder at lower pressures to static disorder at higher pressure. We have also investigated the possibility of proton jumps across the interlayer, by determining the potential energy well along the O···O vector. We infer that proton jumps across the interlayer are either severely limited or highly cooperative since we did not find any evidence for a double well along the O···O vector. The absence of a double well along the O···O vector, the evolution of O-H···O distances with compression, and the gradual transition to a symmetric O-H···O configuration, all argue for weak hydrogen bonding in brucite.

Keywords: High-pressure study, brucite, quantum mechanical calculations, DFT, order-disorder, proton, crytal structure