Cryogenic stabilization of molecular hydrogen in dense cubic ice

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Abstract

Hydrogen storage remains a central challenge for the deployment of hydrogen-based energy technologies, particularly due to the lack of safe and efficient solid-state storage materials operating near ambient conditions. While most strategies rely on porous frameworks or chemically reactive hosts, dense molecular solids have remained largely unexplored. In this work, we demonstrate that cubic ice (I_c), obtained from high-pressure hydrogen hydrates, can retain molecular hydrogen as an interstitial guest upon decompression, establishing a new paradigm for hydrogen storage in non-porous crystalline materials.

Hydrogen hydrates were synthesized at pressures above 3-4 GPa, where water and hydrogen form the fully occupied cubic C2 phase (H_2:H_2O ≈ 1:1). This phase represents a dense, hydrogen-rich structure stabilized by pressure-induced incorporation of H_2 within a hydrogen-bonded framework. Upon rapid cooling and decompression to ambient pressure, C2 transforms topotactically into fully crystalline cubic ice I_c, preserving the parent symmetry (*Fd*-3*m*). This structural continuity enables direct investigation of hydrogen retention mechanisms following release from high-pressure conditions.

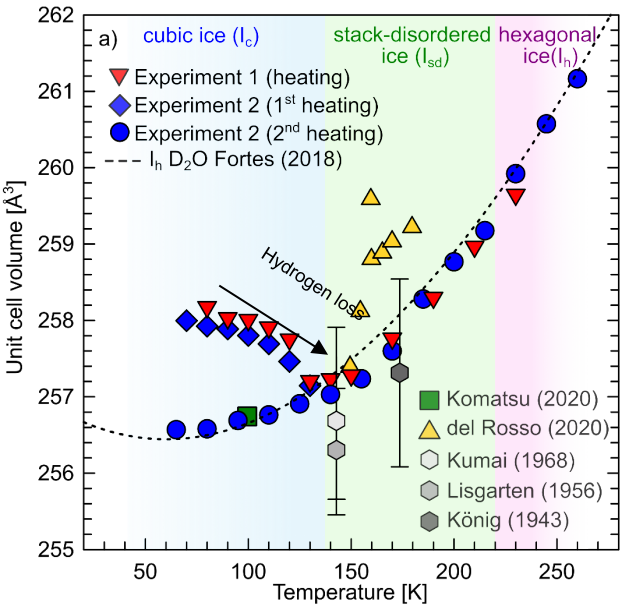

Figure 1. Unit cell volume evolution of cubic ice produced by decompression (to 0.1 MPa) of C2 hydrogen hydrate at low temperature (red and blue symbols) determined *via* neutron diffraction.

Using neutron diffraction, synchrotron X-ray diffraction, and Raman spectroscopy, we observe that the recovered I_c exhibits a reproducible lattice expansion (~0.6% at 80 K) relative to hydrogen-free ice, providing clear evidence for residual hydrogen trapped within the lattice. This expansion progressively vanishes upon heating to ~130 K, indicating gradual hydrogen release. Spectroscopic measurements further confirm the presence of molecular H_2 through characteristic roton and vibron modes, consistent with weakly bound, interstitial hydrogen occupying multiple local environments.

Importantly, moderate pressures (~0.18 GPa) significantly enhance hydrogen stability and reversibility. Under these conditions, remnants of the C2 phase persist up to 90 K, demonstrating that hydrogen-rich hydrate structures can survive far below their nominal stability fields. Moreover, cubic ice can be partially refilled with hydrogen at the same pressure, leading to lattice expansions exceeding 1.5% and confirming pressure-driven re-incorporation of H_2. The hydrogen content retained in I_c corresponds to several percent of the parent hydrate composition, with estimated storage densities comparable to interstitial hydrogen in metals.

These results reveal that pressure not only stabilizes hydrogen-rich hydrate phases but also enables metastable trapping and reinsertion of hydrogen in dense, non-porous crystalline ice. This behavior challenges the conventional view that hydrogen storage requires permanent porosity or strong chemical bonding. Instead, weak host-guest interactions within a dense hydrogen-bonded lattice can sustain significant hydrogen uptake under cryogenic conditions.

Beyond energy applications, these findings have implications for planetary and astrophysical environments, where pressure-temperature cycling and radiation processes may generate similar metastable hydrogen-bearing ice phases. Cubic ice may thus act as a transient hydrogen reservoir in icy moons, comets, and interstellar grains.

Overall, cubic ice emerges as a minimal model system for studying hydrogen-lattice interactions under pressure, highlighting dense hydrogen-bonded solids as a previously unrecognized class of materials for hydrogen storage physics.