A077 **Phase Transitions**

Searching for a hydrogen-ordered counterpart of ice IV through *in-situ* high-pressure powder neutron diffraction experiments

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There are at least 20 ice polymorphs experimentally observed to date. One of the origins of the very rich polymorphism is the presence of hydrogen disorder-order phase transitions. Thanks to the bent structure of water molecules, there are orientational order and disorder in ice crystals, where the space-averaged crystal structures are respectively called hydrogen ordered and disordered. Since hydrogen-ordering transitions induce few changes in the oxygen-atom sublattice, neutron diffraction is essential to distinguish ordered and disordered ice phases by refining hydrogen (deuterium) site occupancies.

Searching for the hydrogen-ordered counterpart(s) of a known disordered parent phase is a successful strategy in recent decades. Ices XIII and XIV, reported together by Salzmann *et al.* in 2006, are the ordered counterpart of ices V and XII, respectively [1]. Another disordered phase ice VI has two different ordered counterparts depending on the pressure at which ice VI is cooled, namely ices XV (Salzmann *et al.*, 2009 [2]) and XIX (Gasser *et al.*, 2021 [3]; Yamane *et al.*, 2021 [4]) with different densities.

Ice IV is a high-pressure metastable phase with a completely hydrogen-disordered crystal structure, but its ordered counterpart has never been reported so far. According to Rosu-Finsen and Salzmann (2021), HCl-doped ice IV produces a weak endotherm in differential scanning calorimetry (DSC) as is quench-recovered to ambient pressure under liquid nitrogen and thereafter heated in a calorimeter [5]. Although this endothermic feature may originate from the order-to-disorder phase transition, other phenomena, such as unfreezing orientational glasses, could also produce such weak endotherms.

As we recognised the importance of crystallographic investigations into this system, we have conducted time-of-flight *in-situ* powder neutron diffraction experiments at the high-pressure neutron diffractometer *PLANET* [6] in Materials and Life Science Experimental Facility of J-PARC. The sample conditions were controlled by a temperature-variable opposed-anvil hydraulic press *Mito system* [7]. Pulsed white neutrons were irradiated through an anvil and scattered neutrons were collected on detectors at $2\theta = 90°$. DCl-doped deuterated water was loaded on the *Mito system* and doped ice IV was prepared by following an established protocol via high-density amorphous ice [8]. To investigate the potential hydrogen (deuterium) ordering, the prepared ice IV was slowly cooled under pressure with neutron diffractograms collected continuously to monitor changes in the lattice parameters. A high-quality profile was recorded at the lowest temperature. The acquired diffraction profiles were analysed in the Rietveld method with *GSAS/EXPGUI* software [9,10].

Tracking unit-cell volume at varying temperatures is a fundamental way to find first-order phase transitions. Interestingly, during slow cooling under pressure, we observed a very small but clear $\partial V/\partial T$ discontinuity in DCl-doped deuterated ice IV, indicating the presence of a corresponding “low-temperature state”. Because there were no peaks that newly emerged at low temperatures, the possible space-group candidates of the “low-temperature state” are the original space group, $R\bar{3}c$, and its only subgroup without changing reflection conditions, $R3c$. Rietveld refinements in $R\bar{3}c$ space group resulted in a completely hydrogen-disordered state, *i.e.* ice IV. Rietveld analysis using the low-symmetry $R3c$ model converged into a slightly ordered structure along the *c*-axis. However, the R factors of these do not differ significantly, making it impossible to conclusively deduce which structural model is better to describe the “low-temperature state” observed in this study. The extremely low degree of hydrogen order is also consistent with ΔS values estimated from the DSC thermograms presented by Rosu-Finsen and Salzmann (2021). Further evidence is desired to better understand these phenomena.

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