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RECONSIDERING PARTIALLY ORDERED STATES OF ICE XV

We all know that water freezes at or below 0°C. But this can only be considered as a fact when the pressure is at one atmosphere. The melting temperature of ice decreases with increasing pressure and reaches its minimum at 0.21 GPa. This was discovered by Gustav Tammann in 1900, who also found two new high-pressure ice polymorphs – ice II and III – from observations of the melting point and density of ice. Despite the fact that it has been more than 100 years since the first findings of ice polymorphs, the discovery and exploration of new polymorphs still continues; very recently, the polymorph ice XVII was discovered (del Rosso et al. 2016).

Why do ice structures have such a rich variety? One of the reasons for this variety could be the order–disorder phenomena of the hydrogen bonds in ice. A single water molecule in an ice structure has four hydrogen bonds to the adjacent water molecules, yielding ${}_4C_2 = 6$ possible hydrogen positions, and the number of possible configurations increases exponentially with an increasing number of molecules. The degree of freedom for such hydrogen configurations contributes to the rich variety of ice structures.

It has long been believed that only one ordered configuration should be allowed as a counterpart of the disordered structure. However, a recent study on ice XV, an ordered phase of ice VI (Fig. 1) that has been investigated by in situ high-pressure neutron diffraction and density functional theory calculations, showed that different kinds of configurations have quite similar free energies, and the observed powder neutron diffraction patterns also indicated a partially ordered state of ice XV (Komatsu et al. 2016). Komatsu et al. (2016) also mentioned that none of the completely ordered configurations is favored; instead, partially ordered states are established as a mixture of ordered domains at the temperatures investigated. This means that the order–disorder pairs in ice polymorphs are no longer one-to-one corresponding pairs, but have one-disorder to *n*-order correspondence, with *n* possible configurations. This mixed ordered configuration scenario also resolves a long-standing contradiction among previous studies of ice XV. Previous neutron diffraction observations have suggested antiferroelectrically ordered structures, which contradicts dielectric measurements and theoretical studies that implied ferroelectrically ordered structures. To be fair, as mentioned in the literature, this idea was already implied by Barclay Kamb in his written more than 40 years ago (Kamb 1973).

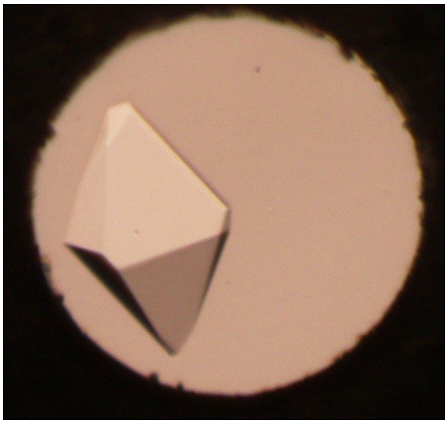

Figure 1 A single crystal of ice VI grown at 0.9 GPa and room temperature (diameter of the gasket hole is 0.3 mm). Ice XV, investigated by Komatsu et al. (2016), is a hydrogen-bond ordered form of ice VI.

Komatsu et al. (2016) also stated that undiscovered different configurations are potentially detectable by neutron diffraction under an electric field and that exploring these will provide new insights into ice physics. The study by Komatsu and colleagues will provide an impetus for additional research for a 'new ice survey', not only for ice XV but also for all other ice polymorphs, which could have a significant impact on the concept of order–disorder phenomena. Finally, it is worth mentioning that the structure of ice XV is still under debate. A neutron diffraction study by Salzmann et al. (2016) stated that the ice XV structure should be derived from a fully ordered structure model. Further experimental and theoretical approaches describing a partially ordered structure will be required for the complete understanding.

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