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CRYSTALS

Ice goes fully cubic

Two independent studies describe the discovery of structurally pure cubic ice I_c made from either ice XVII or a high-pressure hydrogen hydrate.

Christoph G. Salzmann and Benjamin J. Murray

In March 1629, the cleric and scholar Christoph Scheiner witnessed a rare 28° halo from the sun over the ancient city of Rome. More than three centuries later, this observation was suggested to have arisen from the presence of octahedral crystals consisting of cubic ice (ice I_c) rather than the familiar hexagonal ice (ice I_h)[1]. However, despite tremendous research efforts, the preparation of pure ice I_c has remained unsuccessful so far[2]. Now writing in Nature Materials, del Rosso and colleagues report the formation of ice I_c by simply heating ice XVII[3], an unusual low-density form of ice. Simultaneously, Komatsu and co-workers show that ice I_c can also be made by degassing hydrogen from a high-pressure hydrate[4]. The discovery of design principles for making ice I_c opens up a route to the accurate determination of its physical properties and more complex forms of ice I, and it will stimulate new research with respect to a wide range of structurally related materials such as diamond and semiconducting chalcogenides.

… Eighteen phases of ice have been discovered so far at a wide range of temperature and pressure conditions. Hexagonal ice I_h is the low-pressure form of ice that we are all familiar with. Its structure and that of its cubic counterpart, ice I_c, are shown in Figure 1a, b. Both members of the ice I family contain identical layers of hydrogen-bonded water molecules. The structural difference between the two arises from the way that these layers are stacked. In ice I_h, each layer is the mirror image of the previous one, whereas ice I_c is built up by shifting the layers upon stacking. For the best part of the 20th century, it was claimed that ice I_c could be made by, for example, water-vapour deposition onto cold substrates[2]. However, a major leap in our understanding was the realisation that the so-called ice I_c samples were not actually fully cubic but contained hexagonal stacking faults[6]. The structure of such a stacking-disordered ice I (ice I_{sd}) is shown in Figure 1c. In contrast to ice I_h, which shows sharp X-ray diffraction peaks, the irregular stacking in ice I_{sd} leads to diffuse diffraction features mainly around $2\vartheta = 24^\circ$ (see Figure 1d). Computational fitting of such diffraction patterns gives the percentage of cubic stacking, the 'cubicity', for a given sample[7-9]. Up until now, the highest cubicity on record was 78%, a long way from ice I_c, for which the cubicity is 100% [2].

Now two independent studies have described robust means to obtain fully cubic ice I_c. Del Rosso and coworkers show that heating ice XVII under vacuum to 160 K leads to the formation of ice I_c[3]. In addition to diffraction data, the Raman spectrum of the newly discovered ice I_c is presented, which may prove useful for its identification in future studies. Ice I_c was also shown to be slightly lower in density compared to ice I_h. This finding could provide an explanation as to why only ice XVII transforms to ice I_c whereas other ice phases yield ice I_{sd} under similar conditions. Because the density of ice XVII is significantly lower than that of ice I_c, this may enable a mechanistic pathway to ice I_c which is not accessible from denser starting materials. In a separate study, Komatsu and colleagues present an additional way for making ice I_c[4]. Following a completely different approach, the authors first formed C_2 hydrogen hydrate with structural similarity to ice I_c at high pressures. Upon decompression at 100 K, the crystallinity of the sample was lost as the hydrogen gas gushed out from the sample. However, upon reaching ambient pressure, the crystallinity is re-established by the formation of ice I_c. It can be speculated that nanocrystals of ice I_c may have formed during the decompression which then templated the growth of highly crystalline ice I_c at low pressures. Interestingly, despite reporting differences in the thermal stabilities of their ice I_c samples, both studies suggest that stacking-disordered transition states are not important for the transformation of ice I_c to the stable ice I_h upon heating[3 4].

The discoveries reported in these two studies highlight the extraordinary complexity of ice as a material. While one can wonder whether other approaches could lead to the formation of ice I_c, research will now focus on fully characterising and understanding this remarkable new form of ice. Key quantities will be its vapour pressure, heat capacity, heat conductivity and the energy of transformation to ice I_h. These properties will serve as a critical benchmark for testing and improving the various computer models of water. Moreover, given that the type of stacking disorder observed for ice I is also found in a wide range of other inorganic materials, the insights gained from the ice I_c discovery may well highlight important design principles for these materials. Diamond is such an example. While in contrast to ice, the cubic form of diamond is most stable, in recent years, the supposed hexagonal form of diamond, known as lonsdaleite, has been shown to consist of stacking-disordered diamond[10]. The race is now on to make fully hexagonal diamond and the mechanistic findings obtained in the independent studies by Del Rosso and Komatsu and their co-workers might be useful to reach that end. Going back to ice, complex periodic stacking sequences may also exist in addition to extended cubic and hexagonal ice structures. Following the Ramsdell notation, the 4H, 6H and 9R polytypes, for example, are built from periodic $(hc)_x$, $(hcc)_x$ and $(hhc)_x$ segments where 'h' and 'c' indicate hexagonal and cubic stacking, respectively. The corresponding predicted X-ray diffraction patterns are shown in Figure 1d. If and how such high-order polytypes of ice I can be prepared is entirely unclear at present. But it may be that the addition of ice I_c to the ice I family will not be the last. And of course, returning to Scheiner's halo, we still need to find out if there is really ice I_c in the atmosphere of our planet.

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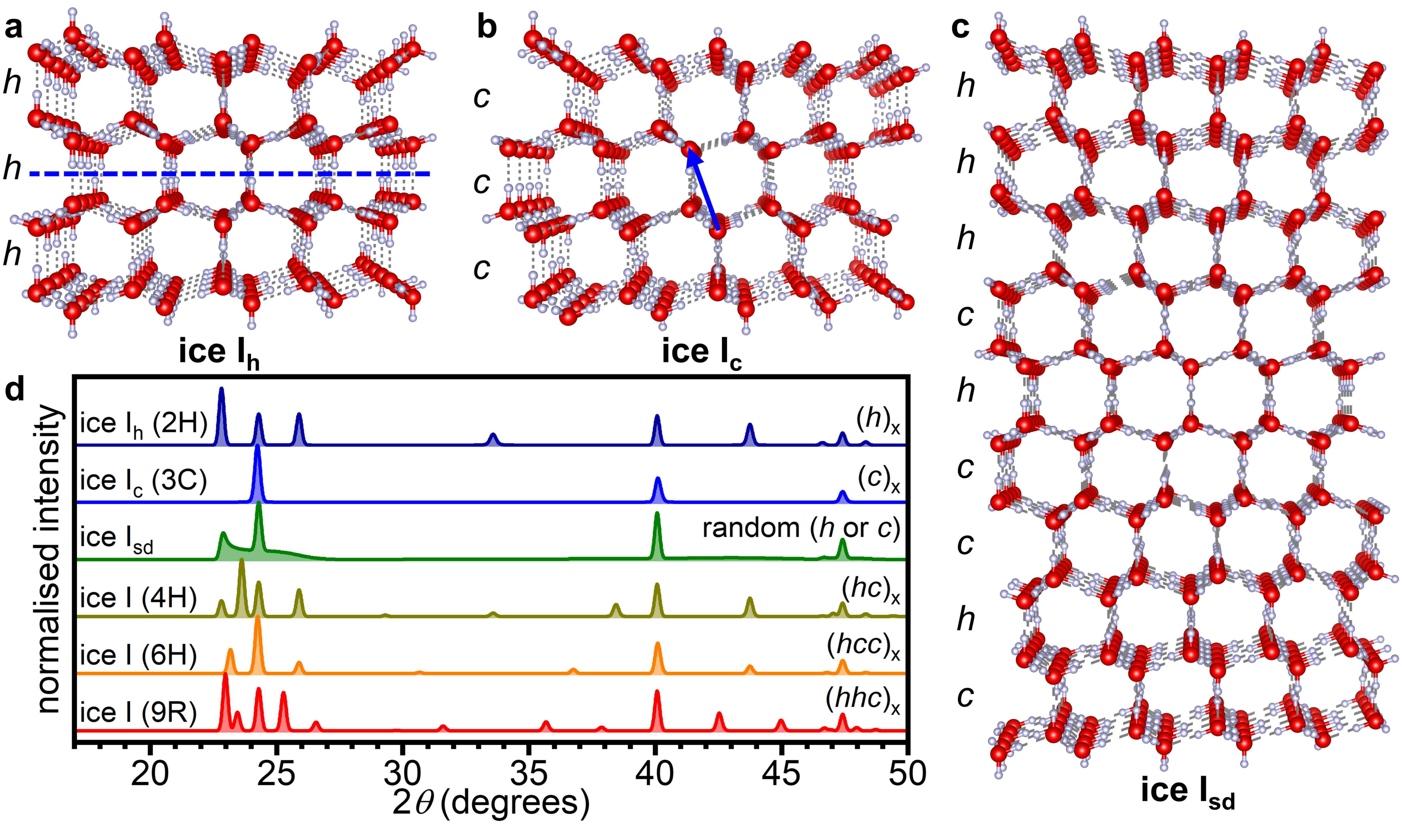
Figure

Figure 1. **Crystal structures and X-ray diffraction of the ice I family**. (a-c) Structures of ice I_h, ice I_c and stacking-disordered ice I (ice I_{sd}). Oxygen and hydrogen atoms are shown as red and white spheres, respectively. The dashed blue line in (a) shows a mirror plane and the arrow (b) is a displacement vector. Hexagonal and cubic stacking is indicated by 'h' and 'c', respectively. (d) Calculated X-ray diffraction patterns (λ = 1.5406 Å) of various ice I structures as indicated by the Ramsdell notation and stacking sequences.



a
h
h
h
ice I_h
b
c
c
c
ice I_c
c
h
h
h
c
h
c
c
h
c
ice I_{sd}
d
normalised intensity
ice I_h (2H)
$(h)_x$
ice I_c (3C)
$(c)_x$
ice I_{sd}
random (h or c)
ice I (4H)
$(hc)_x$
ice I (6H)
$(hcc)_x$
ice I (9R)
$(hhc)_x$
20
25
30
35
40
45
50
2θ (degrees)