a periodic density variation in a system of dysprosium-164 atoms[17,18]. But the droplets in the resulting state were too distant from each other, leading to the loss of frictionless flow.

However, it has been worked out theoretically[19] that, under certain conditions, there is a narrow window in the ratio of dipolar-interaction strength to contact-interaction strength for which the droplets are situated close enough to each other to retain phase rigidity. By tuning an external magnetic field, which changes the way in which atoms scatter when they collide, the authors of the current papers reduced the strength of the contact interaction, bringing all three experiments into the desired parameter regime. The researchers then released the gases from the traps in which they were formed and allowed the matter waves associated with the atoms to interfere with each other. The resulting interference patterns contained a double-peak structure that is a hallmark of supersolidity.

In all the experiments, the peaks were transient phenomena because of three-body losses — losses of atoms that occur when a pair of atoms forms a bound molecular state with the aid of a third collision partner. The lifetimes of the supersolid properties ranged from a few tens of milliseconds for dysprosium-162 and erbium-166 atoms to 150 ms for dysprosium-164 atoms. For the latter atoms, the contact-interaction strength is smaller than the dipole-interaction strength. This feature makes a technically advantageous cooling protocol possible that avoids unwanted excitations and dynamics.

Current limitations of the studies are that each of the experiments involves only a handful of droplets, as well as a complex interplay between the droplets and the axially elongated (cigar-shaped) traps. Future studies should address these issues, aim for a direct manifestation of phase rigidity and study the excitations of a supersolid. Another convincing proof of supersolidity would involve letting a superfluid flow through a prospective supersolid — a situation that is not possible for ordinary fluids and solids. ∎

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PHYSICAL CHEMISTRY

A twist in the tale of the structure of ice

A classic study found that crystalline ice adopts an amorphous form when compressed. Experiments now find that alternative phase transitions can occur — with implications for theories about water's structure. SEE LETTER P.542

JOHN S. TSE

Water is not a simple compound — it exhibits many anomalous physical behaviours that defy adequate explanation. Any fresh information on the structure of water in its various condensed forms is therefore welcome. On page 542, Tulk *et al.*[1] report a study of water under high pressure. They find that it passes through a sequence of crystalline phases rather than forming an amorphous solid, as had been reported by previous studies.

The melting point of ordinary crystalline ice decreases with increasing pressure. This observation inspired a landmark study in 1984, which sought to determine whether such ice would 'melt' when compressed at low temperatures to form a solid that has a disordered molecular structure resembling that of liquid water[2]. Indeed, the study showed that ice compressed at 77 kelvin collapses into a dense form known as high-density amorphous (HDA) ice, which can be recovered at low temperatures under ambient pressure. Remarkably, when heated at ambient pressure, HDA ice transforms into a low-density amorphous (LDA) form instead of reverting to its original crystalline state[3].

Measurements made under conditions of successive compression and decompression have shown that the change in volume associated with the interconversion between HDA ice and LDA ice is discontinuous, and that the transition between these two forms of ice is reversible and does not seem to involve the formation of any intermediate phases[4]. The observations suggest that the interconversion might belong to a class of process known as thermodynamically first-order transitions. If so, this could have important consequences for the phase diagram of water, which relates the temperatures and pressures at which thermodynamically distinct phases of water occur.

The details of the phase diagram of water are not yet fully understood. One possibility is that the boundary between the HDA ice and LDA ice phases extends into, and terminates in, a region of the diagram where water is supercooled (a phase in which water is liquid, despite being below its freezing point). The end of the boundary is known as a critical point. Above the critical point, water would be a mixture of two distinct liquids that have different densities. A feature of this 'two-liquid' model is that compressed ice would form two amorphous solid phases of very different densities that are related to the two liquid waters[5]. Intense experimental and computational efforts have been made to find evidence to support the two-liquid model, including proof of the existence of different amorphous phases in compressed ice.

In general, when a crystalline solid is compressed under 'hydrostatic' conditions that allow thermodynamic equilibrium to be reached, it is expected to transform into another crystalline phase. The formation, instead, of a metastable amorphous phase suggests that an energy barrier has inhibited the transformation of the solid into the second crystalline structure. Such a barrier can be breached if the solid is compressed slowly, which gives time for the structure to relax and for thermodynamic equilibrium to be attained[6]. In this scenario, the formation of the amorphous phase would be described as a kinetic effect, because it depends on the amount of time that is given for a transition to occur.

Ice and the minerals α-quartz and berlinite were the archetypal examples of crystalline solids that become amorphous under pressure. The latter two compounds, however, are now known to transform into crystalline structures when compressed under uniform (isotropic) pressure[7,8]. The pressure-transmitting media used to compress α-quartz and berlinite isotropically are incompatible with water at high pressures; no other suitable pressure transmitter has been available. One study[9] generated quasi-hydrostatic conditions using a pressure
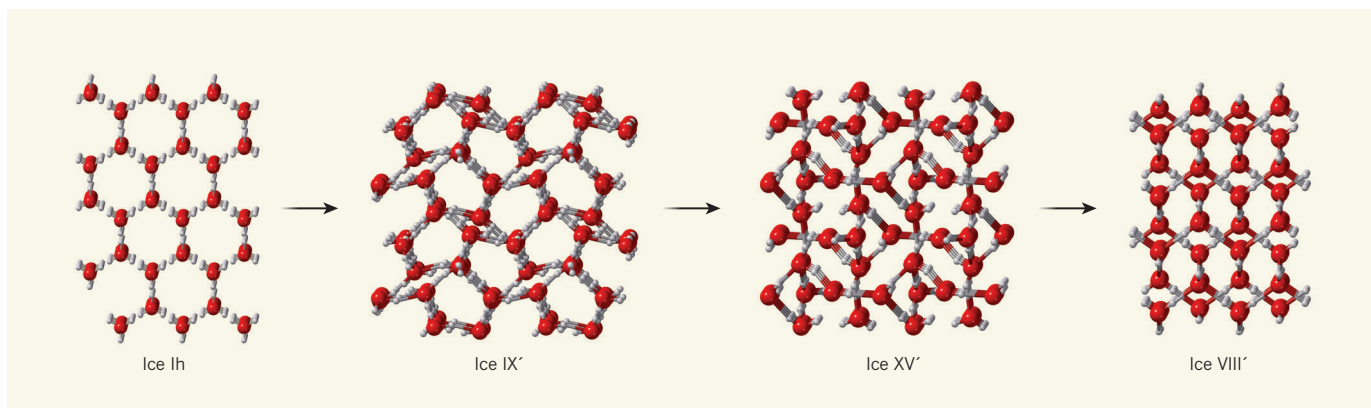
Figure 1 | The transformation of compressed ice into different crystalline forms. Tulk *et al.*[1] report that the normal form of ice (ice Ih) converts sequentially into other crystalline forms (ice IX′, ice XV′ and ice VIII′) at 100 kelvin when pressure is increased in incremental steps, and when the ice is allowed to rest for one hour at each pressure — rather than forming the amorphous solids that were observed in previously reported compression experiments. Red atoms, oxygen; white atoms, hydrogen.

chamber known as a double-sided dynamic diamond anvil cell, and observed the effects on water both with and without a silicone-based pressure-transmitting medium. Ice was seen to change from one crystal form to another before its amorphization, but observations under true hydrostatic conditions were still desirable.

Tulk *et al.* have finally observed the anticipated crystal–crystal transformation of compressed ice under hydrostatic conditions, using neutron diffraction. The authors encapsulated deuterated water in a gasket, which was cooled using boiling liquid nitrogen and placed inside a compression apparatus known as a Paris–Edinburgh press. (Deuterated water contains a heavy isotope of hydrogen, rather than the most abundant isotope, and was used to enhance neutron scattering.) The sample was then compressed in incremental steps, and allowed to rest for an hour at each pressure.

The resulting diffraction patterns show that HDA ice did not form. Instead, the sample sequentially transformed into a crystalline phase known as ice IX′ at 3–7 kilobar, then another crystalline phase (ice XV′) above 10 kbar, and finally into a mixture of ice XV′ and a third crystal form (ice VIII′) above 30 kbar (Fig. 1). These low-temperature phases correspond, respectively, to crystalline phases known as ice III, ice VI and ice VII, which are observed at ambient temperature.

Tulk and colleagues' experiments unequivocally show that, under equilibrium conditions, a 'normal' sequence of crystalline transformations occurs in ice. The HDA ice that was observed in previous studies therefore formed as a result of kinetic effects. Tulk *et al.* were able to observe the crystal–crystal transformations in part because they used a larger sample size than did previous experiments, but also because the long periods between the compressions in their experiments enabled thermodynamic equilibrium to be established, and reduced non-uniformity in the stress that was exerted on the samples during compression.

So, is HDA ice similar in structure to liquid water? There are many lines of evidence to consider. A previously reported analysis of the thermodynamics of ice amorphization showed that the observed pressure at which HDA ice forms from normal ice at low temperatures is much higher than the pressure at which normal ice would be expected to melt at the same temperatures[10]. HDA ice has been found to transform into an even denser amorphous form when heated[11], which shows that it is a kinetic product of rapid compression. And a neutron- and X-ray diffraction study of ice decompressed at constant temperatures found that the transformation of HDA ice into LDA ice involves several intermediate amorphous forms, and is therefore not a first-order process[12]. Computational studies of the molecular dynamics of ice at constant pressure have also been used to reproduce the main characteristics and behaviours of amorphous ice[6]. A theoretical analysis of data from one study suggests that the transformation of ice into HDA ice is not thermodynamically driven, but is instead the result of a type of instability (known as a mechanical or elastic instability) that occurs in certain solids[13]. This result has been confirmed by experiment[14].

> *"The evidence shows that the structure of high-density amorphous ice is not related to that of liquid water."*

The above evidence, taken together with Tulk and colleagues' studies, shows that the structure of HDA ice is not related to that of liquid water. It is a transitional phase that lies between the phases of ice that contain single networks of molecules that are connected by hydrogen bonds (normal ice and ice IX′) and the ice phases that consist of interpenetrating hydrogen-bond networks (ice XV′ and ice VIII′). The substantial reconstruction that is needed to convert single networks into interpenetrating ones requires a large energy barrier to be overcome. At low temperatures, compressed ice therefore initially settles into an amorphous state, but can eventually overcome the energy barrier to form ice VIII′. Thus, the structure of HDA ice is most likely to be a distorted form similar to that of ice XV′.

In light of Tulk and co-workers' results, the assumption that the existence of two amorphous ices that have different densities (HDA ice and LDA ice) supports the two-liquid model of water must be reconsidered. Determining where the boundary between LDA ice and HDA ice fits into water's phase diagram, and whether it extends into and terminates in a 'no-man's land' region of the diagram that has not yet been accessed experimentally[15], and in which only crystal-line ices are expected to form, will be the next experimental challenge. ∎

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