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Annealed high-density amorphous ice under pressure

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The well-known expansion of water on cooling below 277 K is one of several peculiar properties that could signal a second critical point near 220 K and 0.1 GPa in pressure, deep in the supercooled liquid phase. Evidence for this would be a first-order transition line between two distinct supercooled liquids at temperatures below the critical point. As that lies below the minimum crystallization temperature, experimental tests have instead used low- and high-density amorphous ices—LDA and HDA—as proxies for the supercooled liquids. But numerous studies over the past decade have not yielded a clear consensus about the nature of the HDA/LDA transition. Here we identify a previously uncharacterized state of high-density amorphous ice obtained if HDA is annealed at pressures near 2 kbar. The transition between this annealed HDA and LDA is strikingly different from the behaviour found in earlier work, in a way that favours the two-liquid model.

Water has many anomalous properties in the temperature range close to freezing, and in the supercooled range below that, such as the expansion on cooling below 277 K responsible for lakes and seas freezing from the top down. This curious behaviour has been recognized as unusual for at least 300 years, and striking anomalies can be seen in the isothermal compressibility and the isobaric heat capacity, as well as in the coefficient of thermal expansion^{1,2}. These all show a divergence on cooling down to the minimum temperature to which supercooled water can be taken before it freezes—which is about 235 K at ambient pressure (Fig. 1), except on extremely fast timescales³. The hypothesis³ of a second critical point in the region of 220 K and 0.1 GPa to explain this behaviour has become an influential idea in current water science^{2,4}. This two-liquid model entails a first-order transition line between low- and high-density water below 220 K, but that cannot be tested directly because the proposed critical point lies in an experimentally inaccessible region below the minimum freezing temperature (Fig. 1). Instead, evidence for or against the hypothesis has been sought from studies of low-density amorphous ice (LDA) and its high-density analogue, HDA, which are widely taken to be representative of the glassy forms of the liquids¹.

The low- to high-density transition in amorphous ice was first characterized in volumetric measurements by Mishima⁵, which showed a discontinuous density change at ~ 0.3 GPa on upstroke and at 0.05 GPa on downstroke, at 130–140 K (Fig. 1). This indicated a first-order-like transition⁵ with an estimated equilibrium phase boundary at a pressure of ~ 0.15 GPa at 130 K (ref. 6)—continuous with the low-temperature extremum of the proposed line of transitions in the supercooled liquid (Fig. 1). But the first-order nature was uncertain without microscopic characterization of the sample through the transition. This is relatively difficult to achieve under pressure and subsequent work has used HDA brought back, or ‘recovered’, to ambient pressure at 77 K to follow the decomposition to LDA on warming at ambient pressure^{7–14}. The picture has been complicated further by the recent discovery that annealing of HDA under pressures above ~ 0.8 GPa produces an even higher density amorphous form (VHDA)¹⁵, which raises the possibility that the relevant

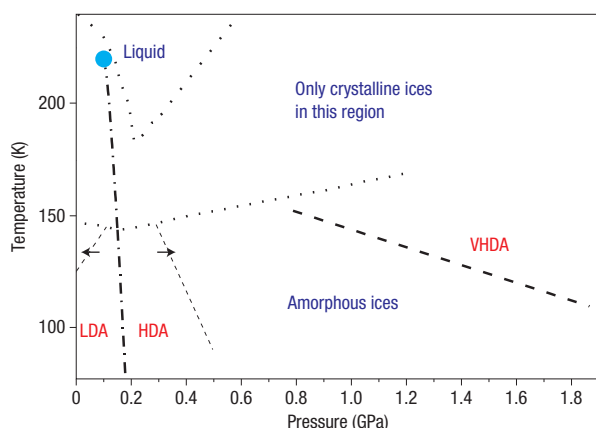


Figure 1 *P*–*T* stability fields of LDA, HDA and VHDA. Dotted lines: (upper) minimum crystallization temperature of (super)cooled water and (lower) maximum crystallization temperature of amorphous ices². Filled blue circle: proposed second critical point and, below this, the (dot-dashed) proposed line of first-order transitions in (inaccessible) water^{2,3}, continuing into the estimated equilibrium phase boundary between LDA and HDA^{5,6}. The arrows show the observed low- to high-density transition at ~0.35 GPa, and reverse transition at ~0.05 GPa back to LDA, at 130–140 K, crossing the upstroke and downstroke lines found by Mishima⁵, shown as thin dashed lines. (On compression, LDA remains metastable up to the upstroke line, and, on decompression, HDA remains metastable down to the downstroke line.) Thick dashed line: approximate *P*–*T* boundary for formation of VHDA (see text).

transition is between LDA and VHDA, not HDA^{16,17}. Two studies have used recovered VHDA as the starting material^{8,12}. (This is not explicit in ref. 12, but the sample was annealed at 1.5 GPa and 150 K, and so must have been VHDA.) In all cases, neutron and X-ray diffraction data^{7–10,13,14} reveal a structural relaxation in the 90–105 K range followed by decomposition of HDA to LDA at temperatures up to ~105–110 K (~5 K higher for VHDA^{8,12}), on the timescale of recent work—that is, 100 min or more. The whole process seems quasi-continuous, with both HDA and VHDA, and there is disagreement as to whether it can be interpreted in terms of an underlying discontinuous transformation to LDA^{7,8} or a continuous process involving intermediate states^{9,10,13,14}. Other studies, using Raman scattering and visual observation, found evidence of two-phase coexistence and argued for a first-order process¹². Thus, this large body of ambient-pressure work has not yet yielded a clear consensus.

We recently carried out neutron diffraction and Raman studies as a function of pressure at 130 K, the conditions of Mishima's volumetric study⁵, and the results indicate a decisively first-order character for the upstroke transition at ~0.35 GPa (Fig. 1)^{18,19}. But, if the transformation crossing the downstroke line at ambient pressure (Fig. 1) really were so different, and even continuous, then the nature of the transition at the equilibrium phase boundary at ~0.15 GPa—and hence the underlying question about a second critical point—would still remain in doubt. We noticed in our data that the high-density amorph formed from LDA on upstroke at 130 K (ref. 18) has a diffraction pattern quite different from that of VHDA and that of unannealed HDA at the same pressure. Therefore, we have carried out diffraction studies of HDA annealed under low pressure. We used neutron methods and a Paris–Edinburgh cell²⁰ (see the Methods section), and our measurements are shown in Figs 2 and 3. We have followed recent ambient-pressure diffraction studies^{7–10,13,14} in using the position (*d*-spacing or $Q = 2\pi/d$) and width of the first diffraction peak (see Fig. 2 inset) throughout to monitor the structural state of the sample.

We find that HDA annealed at 0.2–0.3 GPa to 130 K is like the amorph obtained by compressing LDA at 130 K, and is not VHDA. We have recovered this annealed HDA to ambient pressure at low temperature, and warmed it up to and through the transition to LDA, and observe an abrupt transition at ~128 K rather than the quasi-continuous transformation at ~110 K obtained with unannealed HDA and with VHDA. Thus, we show that, with the same annealed HDA as is involved in the upstroke transition, essentially the same first-order behaviour is obtained in crossing the downstroke line at ambient pressure. And this behaviour is consistent with the two-liquid model.

All of several samples not warmed above 85 K at any time during their formation and recovery to ambient pressure (see the Methods section) had a *d*-spacing of 2.98(2) Å for the first diffraction peak (see Fig. 2 and inset). This agrees with published values where the sample is explicitly shown to have been kept at 77 K and compressed steadily over the timescale of an hour or so^{7,21,22}. We designate this unannealed HDA, as made and recovered at low temperature, u-HDA. We warmed u-HDA at pressures in the range 1.4–2.0 GPa to form VHDA, and the open triangles (green and blue) in Fig. 2 show the change on warming from 85 to 150 K at 1.8 GPa. This and other samples cooled and recovered to ambient pressure at ≤85 K gave a first-peak position of 2.75(2) Å (Fig. 2 and inset)—consistent with the accepted value for VHDA¹⁵.

'EXPANDED' HIGH-DENSITY AMORPHOUS ICE

Our first key finding is that u-HDA and VHDA both transform on warming at low pressures to the same annealed form of HDA, characterized by an increase or expansion of the first-peak *d*-spacing, and that this 'expanded' HDA, or e-HDA, is also what is obtained at the upstroke LDA to HDA transition:

(1) The open green circles in Fig. 2 show the increase in *d*-spacing (decrease in *Q*) as we warmed a u-HDA sample from 85 to 125 K at ~0.11 GPa to form e-HDA (filled red circles). When the pressure was then increased at 125–130 K, the e-HDA *d*-spacing decreased again and coincided with the u-HDA compression line above ~0.6 GPa, as shown by the filled red circles. The first e-HDA peak also sharpened considerably with increasing pressure over this range, and its width is very similar to that of u-HDA at ~0.6 GPa. We detected no pressure increase accompanying the initial expansion of the first-peak *d*-spacing, and we estimate from the characteristics of the Paris–Edinburgh pressure cell that any density decrease must then be less than ~2% (in agreement with density measurements by Mishima⁵ in the same pressure range). The same results were obtained with another sample (not shown).

(2) The behaviours of two VHDA samples (open blue squares) on warming at low pressures are shown. One was warmed from ambient pressure and 85 K to an estimated final pressure of ~0.3 GPa at 130 K (see the Methods section) where its diffraction pattern was identical to that of e-HDA obtained from u-HDA as above. The increase in pressure of ~0.3 GPa accords with the expected initial expansion to HDA-type forms^{12,15,23} in a fixed volume. The second sample was initially not quite fully densified VHDA and was taken to a pressure of 0.3 GPa at 85 K before heating, as shown. This also increased a further ~0.3 GPa by 130 K, to reach the u-HDA (and e-HDA) line at ~0.6 GPa where it had a diffraction pattern like that of both u-HDA and e-HDA at the same pressure. In both cases, the final state is shown as a filled red square to denote e-HDA.

(3) A sample of HDA obtained from the LDA to HDA transition at 130 K, shown by filled red triangles, gave peak positions and widths that are the same within error as in e-HDA and vary with pressure in the same way (Fig. 2).

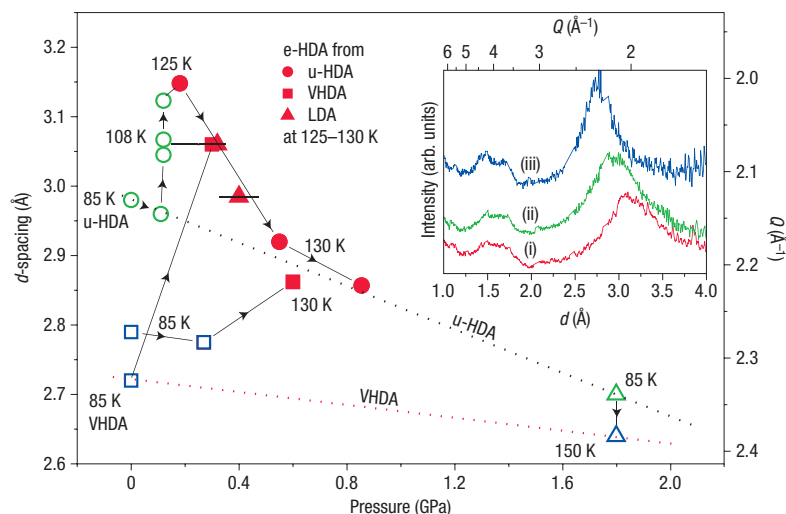


Figure 2 Position of the first diffraction peak in high-density amorphous ices, as a function of P and T . Positions are given as both d -spacing and $Q = 2\pi/d$. Dotted lines: estimated upstroke locus of peak positions for u-HDA (upper) and VHDA (lower) at 85 K. Open green circles: compression of u-HDA to ~ 0.1 GPa at 85 K, followed by annealing to e-HDA on warming to 125 K. Filled red circles: e-HDA at 125 K, then compressed to ~ 0.8 GPa at 130 K. Open blue squares: two VHDA samples, one recompressed at 85 K, and both warmed into e-HDA at 130 K (filled red squares). Filled red triangles: e-HDA made from LDA at 130 K (ref. 18). Open triangles: u-HDA (green) heated to VHDA (blue) at 1.8 GPa. The horizontal bars at 3.06 and 2.98 Å show estimated pressure ranges for the e-HDA from VHDA and from LDA, as discussed in the Methods section. Temperatures, d -spacings and other pressures are determined as set out in the Methods section. Inset: typical diffraction patterns. The first diffraction peak is the one at the largest d -spacing (smallest Q). Sharp diffraction peaks from the lead pressure calibrant and the sintered diamond of the pressure-cell anvils have been removed for clarity. Data are shown for (i) e-HDA at ~ 0.18 GPa and 125 K (plotted in the main figure as a filled red circle), (ii) u-HDA at ambient pressure and 85 K—open green circle, and (iii) VHDA at ambient pressure and 85 K—open blue square at 2.72 Å.

Thus, u-HDA, VHDA and LDA have all been shown to transform at pressures of ~ 0.1 – 0.4 GPa to e-HDA amorphs that have the same diffraction pattern, and we can also conclude that u-HDA anneals to e-HDA on warming below ~ 0.5 GPa and to VHDA above ~ 0.8 GPa. Thus, crucially, it is e-HDA and not VHDA that is relevant to the nature of the transition from LDA and the issue of the proposed second critical point—contrary to the conclusions of Koza *et al.*⁸ and others^{16,17,24}.

e-HDA TO LDA TRANSITION

It is then of interest to investigate the transformation of e-HDA to LDA at ambient pressure. Figure 3 shows results obtained when warming two different e-HDA samples after low-temperature recovery. The data in Fig. 3a were obtained from a sample prepared by annealing u-HDA to 130 K at 0.18 GPa and recovering to ambient pressure at 80 K. The peak positions are shown by filled red circles in Fig. 3c. The recovered peak position of 3.12 Å is close to the maximum value reached by the sample shown expanding in Fig. 2, and there is no discernible shift of the peak on heating until the sample makes an abrupt transition to LDA. Profile (v) in Fig. 3a, collected through a 20-min linear temperature increase from 125 to 128 K, shows e-HDA with the same first-peak d -spacing as in profile (iv) plus a small component of LDA. And the profile (vi) collected a few minutes later was pure LDA. Together these indicate that LDA appeared only in the last few minutes of the temperature increase, close to 128 K, and the transformation then completed rapidly without passing through any detectable intermediate states.

The second sample was annealed to 130 K at 0.30 GPa before recovery, and its warm-up behaviour is shown in Fig. 3b. As expected from the pressure dependence of e-HDA in Fig. 2, the higher pressure at which this sample was annealed leads to a smaller d -spacing on recovery than for the sample annealed at 0.18 GPa.

The peak position (red filled diamonds in Fig. 3c) remains constant to 110 K and then shifts to closely the same d -spacing as the first sample before transforming abruptly to LDA at 123 K.

The difference from the behaviour of u-HDA and VHDA is striking. This is illustrated in Fig. 3c where the open symbols show several previous results for warming up at ambient pressure. These three samples are all nominally u-HDA, although the one used for the X-ray diffraction study of Tulk *et al.*⁹ seems from its initial first-peak d -spacing of 2.79 Å to be transformed to a VHDA-like form¹⁹. Unlike the results obtained from e-HDA, all exhibit a strong, and increasing, expansion of the first-peak d -spacing, that starts below 100 K and continues to an apparent transformation to LDA at temperatures up to ~ 105 – 110 K. Experiments on similar timescales locate the transformation at ~ 5 K higher for VHDA^{8,12}, as already noted, but even that is well below the e-HDA to LDA transition temperature of ~ 128 K. And, crucially, whereas diffraction studies of u-HDA and VHDA transforming to LDA show a single first peak that shifts continuously from its position in the high-density amorph to its LDA position^{7–10,13,14}, it can be seen in Fig. 3a,b that the ambient-pressure transformation from e-HDA to LDA has an abrupt, first-order-like nature. Thus, the behaviour identified in previous ambient-pressure work^{9,10} as revealing intermediate states and a continuous transition is entirely absent when e-HDA is used. Instead, the behaviour shown in Fig. 3a,b is very similar to that found in our study of the upstroke LDA to HDA transition under pressure^{18,19} which shows two-peaked diffraction patterns for intermediate stages, as expected for a first-order transition between an initial and a final state¹⁹.

Recent work by Koza and co-workers^{7,8} throws interesting light on the ambient-pressure behaviour of u-HDA and VHDA. It is shown that u-HDA anneals significantly over a few hours, even at 87 K, and also exhibits further changes, detectable after 10 h at 100 K, that can be well modelled as the onset of a progressive

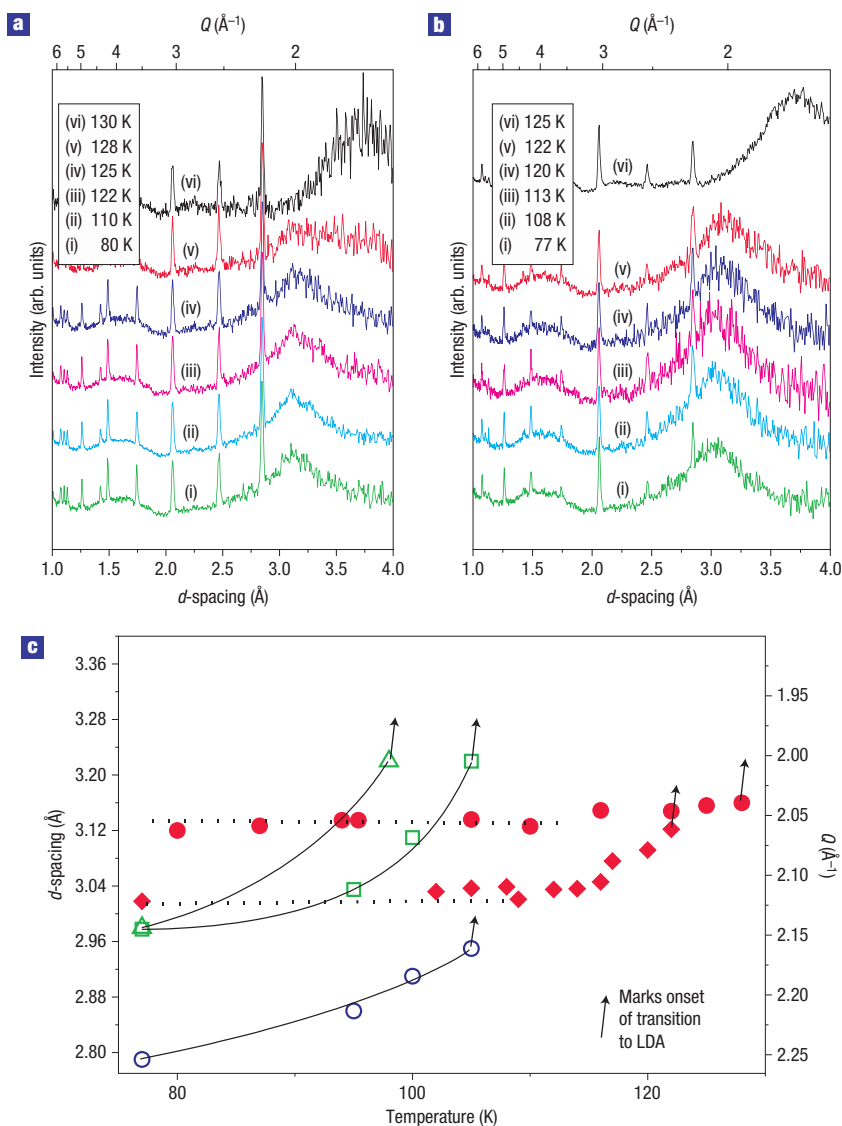


Figure 3 Behaviour of recovered high-density amorphous ices on warming at ambient pressure. **a,b**, Diffraction patterns obtained, at the temperatures given, from e-HDA samples annealed to 130 K at 0.18 GPa (**a**) and at 0.30 GPa (**b**) as they are warmed up to and through the transformation to LDA. Sharp peaks are from the lead pressure calibrant and the sintered diamond of the pressure-cell anvils. **c**, Variation of d -spacing (and Q) of the first diffraction peak, shown by filled red circles for the sample in **a** and by filled red diamonds for the sample in **b**. The open symbols show the behaviour of u-HDA reported in previous work—for samples used in the neutron and X-ray diffraction studies (green squares and blue circles, respectively) of Tulk *et al.*⁹, and for a sample used in the studies of Koza *et al.*⁷ (green triangles). The arrows mark the onset of the transformations to LDA, which has a first-peak d -spacing of 3.7 Å ($Q = 1.7 \text{ Å}^{-1}$) as shown in profile (vi) of panels **a** and **b**. The dotted lines indicate the constancy of the peak position to $\sim 110 \text{ K}$. The solid-line curves through the data points from ref. 9 are guides to the eye; the one for the data points from ref. 7 is taken arbitrarily to be similar in form. Temperatures and d -spacings are determined as described in the Methods section.

nucleation of LDA in the matrix of (unstable) HDA; and VHDA behaves in a similar way but at a slower rate. Thus, ambient-pressure experiments on u-HDA and VHDA will observe a system that is unstable against e-HDA as well as LDA. And responses to both these instabilities increase in rate with increasing temperature and are likely to interact with each other. This makes for a complex, time- and temperature-dependent process.

In contrast, the e-HDA samples are already fully annealed and so are unstable only against LDA. The lack of any significant change in the diffraction pattern of the e-HDA sample in Fig. 3a shows that there is no detectable structural change or nucleation of LDA before the transition in this case, and suggests that this sample provides the closest possible approach to observation of a true HDA to LDA

transition at ambient pressure, with a transition temperature of $\sim 128 \text{ K}$. It seems plausible to interpret the behaviour of the second e-HDA sample as showing a small amount of structural change (but no nucleation) above 110 K (Fig. 3c), before transforming to LDA at $\sim 123 \text{ K}$. The significance of e-HDA is clear; and it is evident that diffraction experiments with u-HDA and VHDA have been obscured by annealing effects.

e-HDA AND VHDA

Our results also modify previous understanding of VHDA by showing that e-HDA and VHDA can be transformed reversibly into each other, and in further experiments on other samples we

have cycled repeatedly between VHDA and e-HDA. An estimated boundary for the formation of VHDA from u-HDA is drawn in Fig. 1, placed (arbitrarily) through the temperatures at which we obtain ~75% of the change in d -spacing from u-HDA to VHDA on warming at 1.0 and 1.8 GPa on multi-hour timescales. This line is also in accord with Mishima's finding that VHDA forms on compression between ~1.2 and 1.5 GPa at ~135 K (ref. 11), and the fact that Loerting *et al.* obtained ~70% densified VHDA by warming to 155 K at 0.84 GPa (ref. 15). (The exact position of the line may depend on the rate of P - T change, and possibly on whether the system is hydrogenous or deuterated.) Recent new work by Loerting *et al.*²⁵ supports this conclusion that VHDA exists stably only at higher pressures, above ~0.8 GPa.

ORIGINAL MEASUREMENTS REVISITED

In his 1994 study, Mishima⁵ mapped out the upstroke and downstroke transition lines marked in Fig. 1, and we have shown how annealing effects have confused or misled numerous subsequent attempts to characterize the transition crossing the downstroke line by warming u-HDA or VHDA at ambient pressure. In retrospect, it is apparent that the principal advantage of our upstroke study^{18,19} was that pressure stabilizes the high-density form, making it possible to work at 130 K, and thus avoid annealing effects. By finding a way to avoid them at ambient pressure too, we have succeeded in crossing the downstroke line correctly, at a temperature that agrees within uncertainties with the ambient-pressure limit of Mishima's line of ~125 K (ref. 5). It should be noted that he crossed this line on warming at pressures below 0.05 GPa (Fig. 3 in ref. 5) and, because his experiments were being done in the 120–140 K range, this will have been e-HDA transforming to LDA, although not recognized as such. Thus, we have finally shown that the upstroke and downstroke transitions are both of a first-order nature in diffraction experiments, and the underlying equilibrium transition at ~0.15 GPa must then also have this character.

A remaining question is the extent to which the amorphous forms are true proxies of the supercooled liquid^{1,14}. We note that the transition between LDA and e-HDA can be observed at ~130 K, which is well above the temperatures previously reached in ambient-pressure studies, and likely to be close to the glass transition temperature on the timescale of our measurements. This possibility is supported by a recent study²⁶ showing that re-orientational relaxation times are of the order of 1–100 s in high-density amorphous ice at 130–140 K, which indicates that it may be an ultraviscous liquid at these temperatures under pressure. Thus, our results make the two-liquid model very plausible, which may have important implications not only for the understanding of water but also for other related fundamental systems such as SiO₂ and Si (ref. 27). Furthermore, promising new perspectives are opened up for both experimental and theoretical enquiry into the nature of the amorphous ices and their relationship to liquid water.

METHODS

EXPERIMENTS AND MEASUREMENTS

Data were collected on the PEARL beamline of the ISIS pulsed neutron source at the Rutherford Appleton Laboratory, UK. Experimental procedures were simplified by working a little above 77 K, and we established that using temperatures up to 85 K made no detectable difference to the results. Our samples were produced by slow compression of 99.9% deuterated D₂O ice Ih at ≤85 K to maximum pressures between 1.6 and 2 GPa, followed by recovery to ambient pressure at ≤85 K. In general, diffraction patterns were collected for

1–2 h. Values of d -spacings were determined to ±0.02 Å (or ~0.015 Å⁻¹ in Q). Temperatures were measured to ±1 K with pre-calibrated K-type thermocouples. Pressures were determined to ±0.04 GPa from the unit cell volume of a lead pressure calibrant using the P - T equation of state developed by Besson *et al.*²⁸.

PRESSURE ESTIMATES WITHOUT A CALIBRANT

There was no pressure calibrant in two of the experiments used in Fig. 2, namely the production of e-HDA from LDA at 130 K, and the production of e-HDA from VHDA at 130 K and ~0.3 GPa. The horizontal bar at 3.06 Å in d -spacing in Fig. 2 indicates the estimated pressure range for the e-HDA made from VHDA, taking account of the known behaviour of other VHDA samples. The point (filled red square) is placed towards the upper end of the range as the first peak width accords with that of e-HDA from both u-HDA and LDA at this d -spacing. The red filled-triangle point at 3.06 Å in d -spacing was obtained from a mixture of LDA and e-HDA part way through the transition at 130 K, and is placed at the transition pressure measured by Mishima⁵ at the same temperature. The red filled-triangle point at higher pressure was then estimated to be in the range indicated (by the horizontal bar) from the known pressure-load behaviour of our Paris–Edinburgh cell.

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References

- Mishima, O. & Stanley, H. E. The relationship between liquid, supercooled and glassy water. *Nature* **396**, 329–335 (1998).
- Debenedetti, P. G. Supercooled and glassy water. *J. Phys. Condens. Matter* **15**, R1669–R1726 (2003).
- Poole, P. H., Sciortino, F., Essmann, U. & Stanley, H. E. Phase-behaviour of metastable water. *Nature* **360**, 324–328 (1992).
- Debenedetti, P. G. & Stanley, H. E. Supercooled and glassy water. *Phys. Today* **56**, 40–46 (2003).
- Mishima, O. Reversible first-order transition between two H₂O amorphs at ~0.2 GPa and ~135 K. *J. Chem. Phys.* **100**, 5910–5912 (1994).
- Whalley, E., Klug, D. D. & Handa, Y. P. Entropy of amorphous ice. *Nature* **342**, 782–783 (1989).
- Koza, M. M., Schöber, H., Fischer, H. E., Hansen, T. & Fujara, F. Kinetics of the high- to low-density amorphous water transition. *J. Phys. Condens. Matter* **15**, 321–332 (2003).
- Koza, M. M. *et al.* Nature of amorphous polymorphism of water. *Phys. Rev. Lett.* **94**, 125506 (2005).
- Tulk, C. A. *et al.* Structural studies of several distinct metastable forms of amorphous ice. *Science* **297**, 1320–1323 (2002).
- Guthrie, M. *et al.* Direct structural measurements of relaxation processes during transformations in amorphous ice. *Phys. Rev. B* **68**, 184110 (2003).
- Mishima, O. Relationship between melting and amorphization of ice. *Nature* **384**, 546–549 (1996).
- Mishima, O. & Suzuki, Y. Propagation of the polymorphic transition of ice and the liquid–liquid critical point. *Nature* **419**, 599–603 (2002).
- Guthrie, M., Tulk, C. A., Benmore, C. J. & Klug, D. D. A structural study of very high-density amorphous ice. *Chem. Phys. Lett.* **397**, 335–339 (2004).
- Tse, J. S. *et al.* Investigation of the intermediate- and high-density forms of amorphous ice by molecular dynamics calculations and diffraction experiments. *Phys. Rev. B* **71**, 214107 (2005).
- Loerting, T., Salzmann, C., Kohl, I., Mayer, E. & Hallbrucker, A. A second distinct structural “state” of high-density amorphous ice at 77 K and 1 bar. *Phys. Chem. Phys.* **3**, 5355–5357 (2001).
- Klug, D. D. Dense ice in detail. *Nature* **420**, 749–751 (2002).
- Giovambattista, N., Stanley, H. E. & Sciortino, F. Relation between the high density phase and the very-high density phase of amorphous solid water. *Phys. Rev. Lett.* **94**, 107803 (2005).
- Klotz, S. *et al.* Nature of the polymorphic transition in ice under pressure. *Phys. Rev. Lett.* **94**, 025506 (2005).
- Klotz, S. *et al.* Reply to Comment on ‘Nature of the polymorphic transition in ice under pressure’. *Phys. Rev. Lett.* **96**, 149602 (2006).
- Besson, J. M. *et al.* Neutron powder diffraction above 10 GPa. *Physica B* **180–181**, 907–910 (1992).
- Bosio, L., Johari, G. P. & Teixeira, J. X-ray study of high-density amorphous water. *Phys. Rev. Lett.* **56**, 460–463 (1986).
- Floriano, M. A., Whalley, E., Svensson, E. C. & Sears, V. F. Structure of high-density amorphous ice by neutron-diffraction. *Phys. Rev. Lett.* **57**, 3062–3064 (1986).
- Mishima, O., Calvert, L. D. & Whalley, E. Melting ice-I at 77 K and 10 kbar—a new method of making amorphous solids. *Nature* **310**, 393–395 (1984).
- Martoňák, R., Donadio, D. & Parrinello, M. Polymorphism of ice at low temperatures from constant-pressure simulations. *Phys. Rev. Lett.* **92**, 225702 (2004).
- Loerting, T. *et al.* Amorphous ice: Stepwise formation of very-high-density amorphous ice from low-density amorphous ice at 125 K. *Phys. Rev. Lett.* **96**, 025702 (2006).
- Andersson, O. Relaxation time of water's high-density amorphous ice phase. *Phys. Rev. Lett.* **95**, 205503 (2005).
- McMillan, P. E., Wilson, M., Daisenberger, D. & Machon, D. A density-driven phase transition between semiconducting and metallic polymorphs of silicon. *Nature Mater.* **4**, 680–684 (2005).
- Besson, J. M. *et al.* Structural instability in ice VIII under pressure. *Phys. Rev. Lett.* **78**, 3141–3144 (1997).

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Competing financial interests

The authors declare that they have no competing financial interests.

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