The relation between high-density and very-high-density amorphous ice

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The exact nature of the relationship between high-density (HDA) and very-high-density (VHDA) amorphous ice is unknown at present. Here we review the relation between HDA and VHDA, concentrating on experimental aspects and discuss these with respect to the relation between low-density amorphous ice (LDA) and HDA. On compressing LDA at 125 K up to 1.5 GPa, two distinct density steps are observable in the pressure–density curves which correspond to the LDA → HDA and HDA → VHDA conversion. This stepwise formation process LDA → HDA → VHDA at 125 K is the first unambiguous observation of a stepwise amorphous–amorphous–amorphous transformation sequence. Density values of amorphous ice obtained in situ between 0.3 and 1.9 GPa on isobaric heating up to the temperatures of crystallization show a pronounced change of slope at ca. 0.8 GPa which could indicate formation of a distinct phase. We infer that the relation between HDA and VHDA is very similar to that between LDA and HDA except for a higher activation barrier between the former. We further discuss the two options of thermodynamic phase transition versus kinetic densification for the HDA → VHDA conversion.

Introduction

The anomalies of liquid water become much more pronounced at low temperatures, in the (deeply) supercooled state and intense research work has focused on this experimentally demanding metastable region of liquid water's phase diagram (for reviews see ref. 1–4). Over the last two decades it became recognized that "supercooled and glassy water are intimately related and that fundamental understanding of metastable water must encompass both its liquid and vitreous states".[4] The supercooled and glassy states of water pose some of the most interesting questions in contemporary condensed matter physics, such as whether a pure substance may have two critical points.[3]

In this review we concentrate on the relation between high-density amorphous ice (HDA) made by pressure-amorphizing hexagonal ice at 77 K,[5,6] and very-high-density amorphous ice (VHDA) recovered at 77 K after isobaric heating of HDA.[7] We will review mainly recent experimental work, simulation studies have been reviewed recently in ref. 4. A discussion of the relation between HDA and VHDA needs to take into account the relation between the low-density amorphous ice (LDA) (obtained from HDA on heating at ambient pressure, ref. 6) and HDA. Because of that we first discuss the latter and then proceed to VHDA and its relation to HDA.

HDA and LDA play a key role in the concept of poly-amorphism of one-component systems. Two scenarios ratio-nalize the known experimental observations: "according to the liquid–liquid phase transition hypothesis,[8–11] the transition between LDA and HDA is a low-temperature manifestation of a first-order transition between two phases of liquid water: low-density liquid (LDL) and high-density liquid (HDL); LDA and HDA are simply the corresponding vitreous forms. The transition terminates at a liquid–liquid critical point".[3] (for recent reviews see ref. 2–4, 12, 13). In the singularity-free scenario, the amorphous states are again LDA and HDA, the vitreous forms of LDL and HDL. However, the transition between LDA and HDA is continuous.[14–16] In the last two decades numerous reports have appeared on polyamorphic phase transitions in liquids and glasses and on liquid–liquid phase transitions of pure substances where the low- and high-density liquid are separated by an energy barrier (for reviews see ref. 17 and 18). Franzese et al.[19] reported a generic mechanism for generating a liquid–liquid phase transition in single-component materials in the liquid state. Their results showed that liquid–liquid phase transition can occur in sys-tems with no density anomaly. Thus, liquid–liquid phase transitions might be a "general phenomenon among a wide range of liquids that must now be incorporated into a new understanding of the liquid state".[18] These liquid–liquid phase transitions are entropy- and density-driven and they are likely to occur at low temperatures, in the supercooled state, where the negative entropy difference of a HDL–LDL transition can be compensated by enthalpy.[17,18] This presents a real challenge for the experimentalist because crystallization has to be avoided.

High-pressure measurements and simulations of liquid Si and Ge (ref. 20 and 21) provided evidence for formation of very-high-density amorphs and their structure factors have been compared with that of VHDA.[22] Benmore et al.[22] con-cluded that "the similarity of the network structure of very-high-density amorphous ice is shown to have close analogues

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in recently reported high pressure forms of liquid Si and Ge". Furthermore, *in situ* studies of pressure–densification of SiO_2 glasses indicated "the existence of at least two pressure-induced phase transitions".[23] Thus, the study of VHDA and its relation to HDA seems to be of general relevance for understanding the liquid–liquid phase transitions of one-component systems.

One of the main issues in the current debate on polyamorphism of water is how LDA, HDA and VHDA are related to each other. Mishima *et al.*[5] have shown already in their first report of pressure amorphization of hexagonal ice (ice I_h) by X-ray diffraction patterns that HDA transforms on heating at ambient pressure irreversibly in stages (Fig. 5 in ref. 5) and that on heating HDA "a continuous range of phases, as characterised by their density, can therefore be made having densities at zero pressure in the range 1.17–0.94 g cm^{-3}" (reviewed by Whalley in ref. 24). Lately a lot of effort has been put into studying amorphous ices *at ambient pressure* (*e.g.* ref. 25 and 26). Mishima *et al*'s findings[5] have been confirmed by other groups and studied in more detail, and it has been shown by X-ray and neutron diffraction that HDA transforms on heating at ambient pressure or *in vacuo* to LDA through a series of metastable intermediates.[26–29] While studies at ambient pressure are certainly important, it was recently pointed out[30] that it is difficult to judge from these experiments on the nature of phase boundaries located at elevated pressures. Detailed knowledge of all stable and metastable phases found within the relevant pressure–temperature regions is necessary in order to fully understand the transition mechanisms.[31] A direct observation of the phenomena linked to polyamorphism of ice *at elevated pressures* provides, therefore, more direct insight into the nature of the transitions. Because of that, we concentrate in this review on studies performed *in situ* at elevated pressures.

The structural states of the amorphous ice forms have been named in recent publications in various ways and confusion can arise from that practice. We follow the practice used in our ref. 32 and restrict in the following the term HDA for the amorphous ice formed on compression of ice I_h at 77 K either under pressure or recovered at 1 bar,[5,6] and the term VHDA to the structural state obtained after isobaric annealing at $\geq \sim 0.8$ GPa *and* recovering at 77 K and 1 bar.[7]

The LDA → HDA transition

Mishima, Calvert and Whalley first showed in 1984 that application of pressure to hexagonal ice (ice I_h) at 77 K leads to the formation of HDA starting at *ca.* 1.0 GPa.[5] They observed a sudden and sharp transition by monitoring the piston displacement in a piston cylinder apparatus. On release of pressure HDA remains at 77 K a dense solid (1.17 ± 0.02 g cm^{-3}, ref. 5) and it requires heating up to *ca.* 120 K for transforming irreversibly to LDA (0.94 ± 0.02 g cm^{-3}). X-ray powder diffractograms of recovered HDA show a broad diffraction peak centered at ~3.0 Å which indicates that an amorphous state has indeed been produced by increasing the pressure on a crystalline material. This represented the first demonstration of the process of "pressure induced amorphization". The same authors reported in 1985 that LDA trans-

forms on compression at 77 K to HDA starting at *ca.* 0.60 GPa.[6]

For demonstration we show in Fig. 1 piston displacement (right ordinate) *versus* pressure curves of samples pressurized at 77 K in the same manner reported first by Mishima *et al.*[5,6] On compression of ice I_h (solid line) a sudden piston displacement starts at a nominal pressure of *ca.* 1.0 GPa, indicating transition to a denser solid, whereas on compression of LDA (dashed line) this starts already at *ca.* 0.6 GPa. For calculation of the corresponding changes in molar volume (left ordinate) see legend to the figure. On release of pressure at 77 K, the piston does not go back to the position before compression indicating that HDA does not convert back to ice I_h or LDA. Thus, at 77 K pressure–amorphization is not a reversible process. According to X-ray diffraction both routes produce within the experimental uncertainty the same final state recovered at 1 bar and 77 K, namely HDA.[24] However, this has
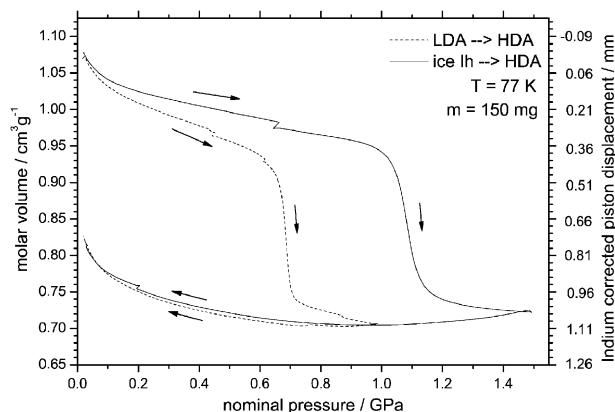

Fig. 1 Compression and decompression of ice I_h (solid line) and of LDA (dashed line) at 77 K as shown by piston displacement (right ordinate, for ice I_h compression and indium corrected) *versus* nominal pressure plots. 150 mg samples were compressed in a piston-cylinder apparatus with 8 mm inner diameter. The samples were kept in a container carefully designed of 0.241 g indium and of the same shape in order to exclude artifacts produced by different amounts and shapes of indium. Indium is required to prevent sudden pressure drops accompanied by shockwave heating causing crystallization of HDA to ice XII.[85,86] The kinks, *e.g.* at *ca.* 0.65 GPa in the ice I_h → HDA compression curve, are caused by minor pressure drops, but these do not lead to formation of ice XII.[86] LDA was made directly in the "universal testing machine" by pressure–amorphizing first ice I_h to HDA at 77 K up to 1.5 GPa and by transforming subsequently HDA to LDA by heating up to 143 K at 0.025 GPa. The experiments were done in a computerized (software TestXpert V7.1) "universal testing machine" (Zwick, model BZ100/TL3S) with a positional reproducibility of ±5 μm and a spatial resolution of 0.01 μm. The samples were compressed and decompressed at a rate of 7000 N min^{-1} (140 MPa min^{-1}). The signal due to the piston-cylinder apparatus lined with 0.241 g indium (and no ice sample) was subtracted as a baseline from the raw pressure-displacement data. The molar volume (left ordinate) was calculated by using densities of 0.935 g cm^{-3} for ice I_h at 77 K,[87] and of 0.94 g cm^{-3} for LDA.[6] In the decompression curve of the ice I_h → HDA transition, $dV/dP > 0$ above *ca.* 0.8 GPa. We note that in Mishima's decompression curve (*cf.* our Fig. 2 and ref. 45) dV/dP is close to zero above *ca.* 1 GPa. We believe that in both curves the procedure for correcting the volume change caused by indium may produce this artifact.

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also been questioned on the basis of density and ultrasonic velocity data.[33]

Since these pioneering studies by Mishima et al.[5,6] numerous reports of the properties of HDA have appeared. The LDA ⇔ HDA transition has been characterized among others by diffraction,[5,6,22,27,29,30,34–42] change of volume,[6,43–45] heat effects,[43,44,46] Raman spectroscopy,[25,47–50] ultrasonics and thermal conductivity,[51–55] visually,[25,56] and by simulations (refs. 42, 57–66, with references for older literature). HDA has been considered to be a glassy state of high-pressure liquid water,[5,6,44,45,67–69] or a collapsed "ill-crystalline" phase,[70,71] and discussions about these interpretations continue (reviewed in ref. 2–4, 12, 13). Its structure has been argued to be similar to that of high-pressure liquid water which suggests that it is a glassy form of the latter.[12,69] The glass-to-liquid transition of emulsified HDA has been suggested to be around 0.4 GPa and 160 K from thermal effects on decompression[46] or, in conflict with this, at <140 K both at 0.4 GPa and 1.0 GPa from dielectric relaxation spectroscopy.[72]

In this discussion of LDA and HDA and their relation, Mishima's report that the LDA → HDA transition can be made reversible at higher temperatures became very important.[45] In Fig. 2 we show the relevant part of Mishima's Fig. 2 in ref. 45, that is the reversible transition between LDA and HDA between 130–140 K. At these temperatures the pressure required for the transition from LDA to HDA is only ca. 0.3 GPa, in contrast to ca. 0.6 GPa at 77 K.[6] The sharpness and reversibility of the transformation is consistent with a first-order transition between LDA and HDA.[4] Hysteresis is pronounced but this is to be expected for a first-order phase transition at low temperatures. Further support for the notion of a first-order phase transition comes from observation of a well-defined propagating phase boundary on transition of HDA (in fact VHDA according to preparation, see next
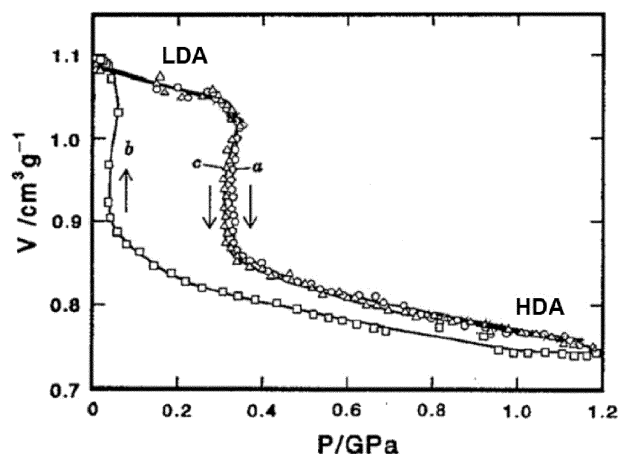
paragraph) to LDA.[25] Recently Klotz et al.[40] reported that the transformation between LDA and HDA is consistent with a first-order transition by in situ neutron diffraction studies at ca. 0.3 GPa and 130 K, which show that all states in the conversion process can be expressed as a linear combination of LDA and HDA. However, Tse et al. subsequently emphasized that X-ray rather than neutron structure factors are required to answer this question unambiguously.[42] Stal'gorova et al.[51] also challenged the first-order view by showing that the density increase (as well as the travel time of an ultrasonic pulse) during the LDA → HDA transformation varies linearly with time, whereas an exponential variation would be expected for a first-order transition. Furthermore, it has been reported that HDA transforms on heating at ambient pressure or in vacuo to LDA through a series of metastable intermediates.[26–29] Thus, the case of a first-order transition between LDA and HDA is still under debate.

The HDA → VHDA transition

The discussion of LDA and HDA and their relation, became even more confusing when Loerting et al.[7] reported in 2001 that an apparently distinct form of high-density amorphous ice can be recovered at 77 K and 1 bar, after isobaric heating of HDA under pressure (reviewed by Klug in ref. 73). Its density is higher than that of HDA made at 77 K (1.25 ± 0.01 g cm^{-3} versus 1.17 ± 0.02 g cm^{-3}) and because of that it has been labelled very-high-density amorphous ice (VHDA). Specifically, HDA was heated at 1.1 GPa from 77 K up to ca. 165 K, or at 1.9 GPa from 77 K to ca. 177 K (cf. Fig. 1 and 3 in ref. 7). According to X-ray diffraction and Raman spectroscopy of VHDA recovered at 77 K and 1 bar, the densified material relaxed on decompression at 77 K to the same structural state. The broad X-ray diffraction peak centered at ∼3.0 Å in HDA shifts to ∼2.75 Å in VHDA and the decoupled O–D peak frequency shifts from 2466 cm^{-1} in HDA to 2484 cm^{-1} in VHDA.[7] The detailed structure of recovered VHDA has been determined by Finney et al.[74] via neutron powder diffraction with isotope substitution, with site–site radial distribution functions and spatial density distributions calculated by the empirical potential structure refinement Monte Carlo procedure.[4] This study showed that the structural change from HDA to VHDA is caused by an additional water molecule occupying an interstitial tetrahedral site, i.e., that the number of nearest neighbours of a central water molecule increases from 5 in HDA (ref. 37) to approximately 6 in VHDA.[74]

We emphasize that Mishima[67] had reported already in 1996 that HDA ices heated or annealed to 130–150 K at 1.0–1.5 GPa "show identical X-ray patterns (with a halo peak around 2.75 Å)". It has been argued, though, that HDA and VHDA are in the same "megabasin" on the potential energy hypersurface and therefore a distinct nomenclature is not necessary. Debenedetti[4] recently concluded that one of the key unanswered questions in amorphous water research is the relationship between VHDA and HDA, that is "whether it is a distinct phase, separated from HDA by a first-order transition, or whether it is simply very dense HDA".

Since Loerting et al.'s[7] first report of VHDA numerous studies of VHDA and its relation to HDA have appeared.

Fig. 2 Compression of LDA to HDA (a), successive decompression and conversion of HDA to LDA (b) and recompression and conversion of LDA to HDA (c) during warming from 130 to 140 K. The sample was compressed and decompressed at a rate of ca. 0.6 GPa min^{-1} (from ref. 45 with changes). The pressure/temperature conditions for these amorphous states to remain intact without crystallizing are given in ref. 88 where the effect of heating rate and pressure on the crystallization kinetics of amorphous ice on isobaric heating between 0.2 and 1.9 GPa is reported.

Ref. 58–66, 75, 76 list recent simulation studies of VHDA and ref. 22, 32, 41, 54, 72, 77–80 list experimental studies. The consensus of the simulation studies on VHDA seems to be that it is a relaxed form of HDA obtained on heating and annealing of HDA under pressure and that VHDA should be considered as the amorphous ice associated with HDL rather than HDA. However, HDA and VHDA were also attributed to distinct phases, called phase III and phase IV, in computer simulation studies of various water potentials with three liquid–liquid phase transitions.[59,63]

We recently repeated Mishima's experiment (Fig. 2 and ref. 45), using improved instrumentation and temperature control. We found that on compressing LDA at 125 K up to 1.5 GPa, two distinct density steps accompanied by heat evolution are observable in pressure–density curves (Fig. 1 in ref. 80). Fig. 3 shows compression of LDA at 125 K up to a nominal pressure of 1.5 GPa at a rate of 20 MPa min^{-1} (dashed line). The density of the sample experiences two pronounced steps of 20% (from 0.94 to 1.13 g cm^{-3}) at 0.45 GPa and of 5% (from 1.22 to 1.28 g cm^{-3}) at 0.95 GPa, respectively. Both density steps are accompanied by heat production, which ceases in the plateau regions following the density jumps. The temperature of the cylinder is generally constant within ± 0.5 K of 125 K and to within ± 2 K during transformations.

We further characterized in separate experiments the structural states labelled in Fig. 3 as HDA and VHDA, by quenching samples at 0.7 GPa (solid line) and at 1.5 GPa (dashed line) to 77 K, by releasing at 77 K the pressure at a rate of 20 MPa min^{-1} fully and by recording the X-ray diffractograms of the recovered phases. These are shown in Fig. 4, together with that of the starting material LDA. The VHDA pattern with the first broad maximum at 2.75 Å ($2\theta = 32.5°$) is indistinguishable from the VHDA pattern reported by us previously.[7] The X-ray pattern labelled HDA resembles HDA on pressurizing ice I_h at 77 K.[7]

The densities of the phases recovered after the first and second density jumps amount to 1.17 and 1.30 g cm^{-3}, respectively, which is close to the bulk densities of HDA and

VHDA at 77 K and 1 bar.[5,7] The increase of densities of the recovered states of 27 and 11% is the increase expected for the LDA → HDA and HDA → VHDA transformations. We conclude, therefore, that VHDA formation upon pressurization at 125 K occurs according to the stepwise sequence LDA → HDA → VHDA. At lower temperatures, e.g. 100 K, the HDA → VHDA transformation does not take place. At higher temperatures, e.g. 150 K, LDA crystallizes. This is, to the best of our knowledge, the first unambiguous observation of a stepwise amorphous–amorphous–amorphous transformation sequence for all systems known to show polyamorphism, with the tetrahedral arrangement being preserved.[18] We note, however, that El'kin et al.[23] inferred in their in situ study of the mechanism of formation of pressure-densified SiO_2 glasses "the existence of at least two pressure-induced phase transitions accompanied by structure rearrangement", where in the first transition the tetrahedral short range structure is still preserved, but in the second transition it is accompanied by a change in the silicon coordination from tetrahedral to octahedral.

We further checked whether the stepwise formation of VHDA from LDA at 125 K depends on the rate of compression and conducted additional sets of experiments at rates of 6, 600 and 6000 MPa min^{-1}.[80] In Fig. 5 the corresponding pressure–density curves are shown in the top panel together with the slopes of these curves in the bottom panel. In all cases the pressures at the density steps are found to be at 0.45 ± 0.02 GPa and 0.95 ± 0.05 GPa, with no dependence on compression rate. Whereas the first densification step of ca. 20% is almost independent of the compression rate, the second step drops to ca. 1% at compression rates of ≥ 600 MPa min^{-1}. Despite this drop, the samples recovered after compressing at 600 MPa min^{-1} are VHDA as evidenced by the X-ray
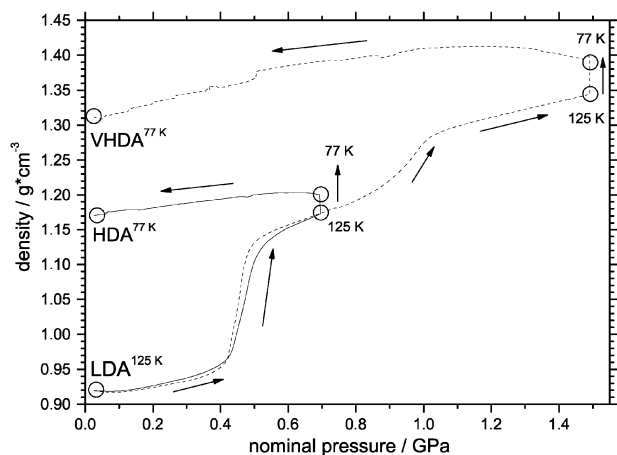

Fig. 3 Pressure–density curves for isothermal compression of LDA at a rate of 20 MPa min^{-1} at 125 K, subsequent quenching to 77 K and decompression at 20 MPa min^{-1}. For calculation of density and further experimental details see ref. 80 (from ref. 80 with changes).
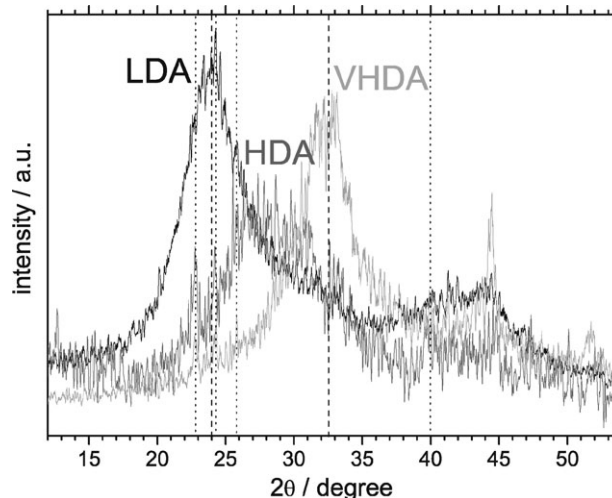

Fig. 4 Powder X-ray diffractograms for the samples labelled LDA, HDA and VHDA recovered at 77 K. Curves are shown on the same scale, smoothed and offset for clarity. Dashed lines are intended to guide the eye to the location of the maximum of the first broad diffraction peak. The dotted lines indicate positions of reflections caused by traces of ice I_h, which had formed by condensation of water vapour during transfer of the sample onto the precooled X-ray sample holder (cf. ref. 88 for details) (from ref. 80 with changes).
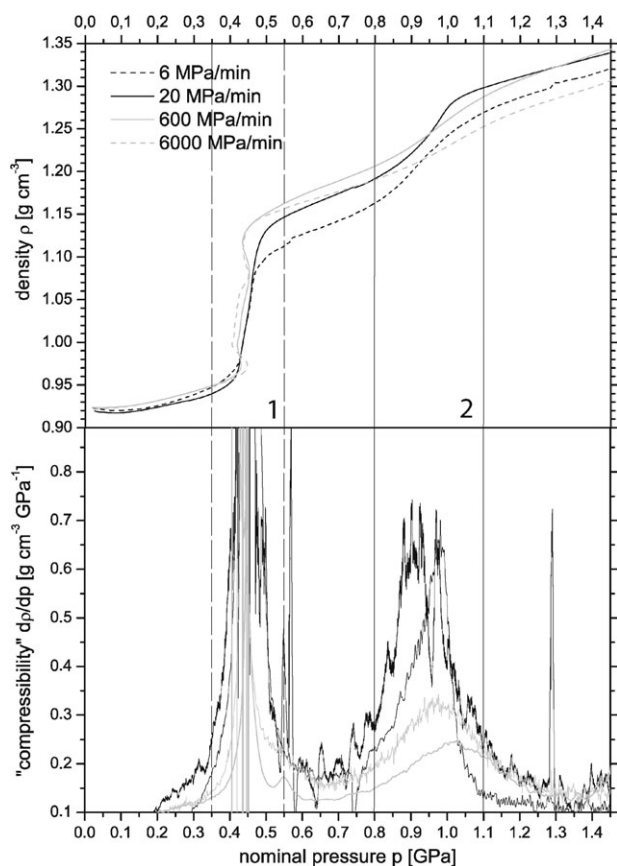
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Fig. 5 Top: Effect of compression rate on pressure–density curves for isothermal compression of LDA at 125 K. The protocol is analogous to the procedure described for Fig. 3 (and for Fig. 1 in ref. 80) using compression rates of 6, 20, 600 and 6000 MPa min⁻¹. The rate of 600 MPa min⁻¹ matches the rate employed in ref. 45. Bottom: Change of density with increasing pressure (first derivative of curves in top panel). Areas of inelastic compression where the change exceeds 0.20 g cm⁻³ GPa⁻¹ are numbered 1 and 2. (From ref. 80 with changes.)

diffractogram (not shown) and the density of 1.30 ± 0.02 g cm⁻³ after decompression. This density value was determined *via* changes of piston displacement in two separate experiments, namely the one containing sample and indium, and a second one with indium only. We believe that our previously reported density value for VHDA at 77 K and 1 bar of 1.25 ± 0.01 g cm⁻³ is more accurate because it had been determined by buoyancy.

The compression curves of Fig. 5 (top) do not collapse after formation of HDA, *e.g.* at 0.65 GPa, in the manner shown by Fig. 2. This is an effect of the variation of the compression rate. With the same compression rate of 20 MPa min⁻¹, the same amount of indium (0.351 g) and of water (0.2995 g), the reproducibility of the change of piston displacement (without correcting for indium) was found to be 0.93 ± 0.04 mm for the first step and 0.25 ± 0.02 mm for the second step in three experiments. The reproducibility of the nominal pressure at the steps is ± 0.02 GPa. Error in the density *vs.* pressure plots shown in Fig. 5 (top) is introduced in addition to the pure statistical error also by the procedure of correcting for indium. Taking together these errors, it is likely that even though the

compression curves do not collapse, *e.g.* at 0.65 GPa, they correspond at this pressure to the same, unique HDA state.

It might seem surprising that the stepwise formation of VHDA has not been already observed in previous studies, as one of the referees had pointed out. Regarding Mishima's important experiment for demonstrating the "reversible first-order transition between two H₂O amorphs at *ca.* 0.2 GPa and *ca.* 135 K" (*cf.* Fig. 2 in ref. 45), our compression rate of 600 MPa min⁻¹ is the same rate used by Mishima. At this rate, the second step flattens out. In addition, the signal-to-noise ratio is higher in Fig. 3 than in Fig. 2 of ref. 45 which helps considerably in elucidating the second densification step. Both aspects explain why Mishima did not observe the second step at higher pressure. Furthermore, the recently reported Raman spectroscopic study of the LDA → HDA → ice VII transitions with increasing pressure at 135 K (*cf.* Fig. 4 in ref. 31) did not show the stepwise HDA → VHDA formation because in the relevant pressure region spectra are shown only at 0.3, 0.5 and 1.3 GPa. Spectra at much smaller pressure increments are necessary in order to detect the stepwise HDA → VHDA formation in this way.

From the change of the second density step in going from 20 to 600 MPa min⁻¹ and the broader pressure range of densification, we estimated that the time required to transform HDA to VHDA is on the order of 10 min at 125 K and 0.95 GPa, which corresponds to the time required to sweep the transformation pressure range at 20 MPa min⁻¹. On the other hand, the transformation time from LDA to HDA must be at least an order of magnitude faster at 125 K since the first density step barely changes even at the highest compression rate employed. The transformation from LDA to HDA and also that of HDA to VHDA, is best described as a "thermally activated process, whose rate increases with increase in the pressure",[81] and thus our findings imply that the activation barrier between LDA and HDA is considerably lower than the activation barrier between HDA and VHDA. Koza *et al.*[79] also concluded recently in a study at ambient pressure that the activation energy for VHDA → LDA is at least 20 kJ mol⁻¹ higher than for HDA → LDA. This higher activation barrier was also found by differential thermal analysis (Fig. 4 in ref. 67): *ca.* 125 K are required to transform HDA annealed under pressure ("VHDA") to LDA, whereas only *ca.* 115 K are required to transform unannealed HDA ("HDA") to LDA. The much faster kinetics of HDA → LDA implies for the reverse transformation sequence VHDA → HDA → LDA that it is very difficult to isolate and characterize HDA simply because it rapidly transforms to LDA once formed from VHDA. Because of that, it will be very difficult to demonstrate reversibility of the HDA → VHDA transformation in the same manner reported by Mishima for the LDA → HDA transformation (Fig. 2 and ref. 45). However, Koza *et al.* (Fig. 1 in ref. 79) succeeded to demonstrate the reversibility by recording an intermediate HDA-like state, with a structure factor indiscernible from that of HDA, by using the fast *in situ* neutron scattering technique during isobaric annealing of VHDA at 113 K. That is, both the HDA ⇔ VHDA and LDA ⇔ HDA transformations are reversible in principle—still they are difficult to be observed together because of the low temperatures and the different activation energies.

So far the HDA → VHDA transition was studied *in situ* at a constant temperature by increasing the pressure. An alternative approach is to increase the temperature at a constant pressure and to study *in situ* changes of density. Fig. 6 demonstrates the latter approach where *in situ* density values of amorphous ice obtained between 0.3 and 1.9 GPa and 144 to 183 K are shown.[32] Starting from HDA made by pressure-amorphizing ice I_h at 77 K, samples were heated at a constant pressure until crystallization to high-pressure ices occurred. Densities of amorphous ice were calculated from those of high-pressure ice mixtures and the volume change on crystallization (*cf.* ref. 32 for details). The most surprising aspect of this study of isobaric annealing is a pronounced change of slope in the *in situ* density *versus* pressure plot at *ca.* 0.8 GPa (Fig. 6): below *ca.* 0.8 GPa the slope is 0.21 g cm^{-3} GPa^{-1}, above *ca.* 0.8 GPa the slope decreases to 0.10 g cm^{-3} GPa^{-1}. Parallel studies of recovered annealed samples by Raman spectroscopy and X-ray diffraction show that irreversible structural changes on isobaric annealing are most pronounced below *ca.* 0.8 GPa, whereas above that pressure only minor structural changes occur. Furthermore, increase of annealing temperature or time had no effect, thus indicating that the samples are fully relaxed. We concluded in ref. 32 that mainly irreversible structural changes below *ca.* 0.8 GPa lead to the pronounced increase in density, whereas above *ca.* 0.8 GPa the density increase is dominated to a large extent by reversible elastic compression. The slope of 0.10 g cm^{-3} GPa^{-1} above 0.8 GPa is the same value as that determined independently for VHDA's elastic densification (see below and ref. 80). This

indicates that above *ca.* 0.8 GPa the structural state obtained on isobaric annealing of amorphous ice is that of VHDA densified further by elastic compression. Furthermore, we are confident that these *in situ* density values are the most accurate ones reported in the literature and that these values should be used as reference in simulation studies of high-density amorphous ice and the effect of annealing on density.

Klotz *et al.*'s[41] recent *in situ* neutron diffraction study of high density amorphous ice under pressure seems to be in conflict with our results,[80] and thus needs to be discussed. They reported that high density amorphous ice at 0.7 GPa and 100 K has about the same O–O correlation function as recovered VHDA at 77 K and 1 bar reported by Finney *et al.*[74] (*cf.* Fig. 4 in ref. 41 for this comparison). They then concluded that this indicates "that the basic mechanism of densification in VHDA (occurring between 100 and 160 K) is the same as the pressure-induced densification at 100 K and that the structures up to the second-neighbour distances are essentially identical".[41] In our recent study of pressure-induced HDA → VHDA transition we found that this transition does not take place at 100 K (*cf.* above) and that it needs 125 K in order to observe formation of VHDA between 0.80 and 1.10 GPa in the form of a distinct densification step (Fig. 5).[80] The pressure of 0.7 GPa is given in ref. 41 with an accuracy of ±0.1 GPa and thus the upper-bound value of 0.8 GPa is the pressure where according to our Fig. 5 irreversible inelastic densification towards the structure of compressed VHDA starts. The time scale of the experiment in ref. 41 (measurement time of *ca.* 10 h and slow compression at a rate of 1 GPa h^{-1}) is much longer than our time scale (*cf.* Fig. 5, compression rates of between 6 MPa min^{-1} and 6000 MPa min^{-1}). Despite the differences in time scale, 100 K seems to be too low for formation of VHDA, even on long time scales, in particular, since D_2O was used in ref. 41 whereas H_2O was used in our study.[80] Exchange of H_2O by D_2O leads for most transitions to an increase in temperature by *ca.* 4–5° for a given pressure, or to an increase in pressure for a given temperature. Thus we would expect for the second density step in our Fig. 3 that on exchange of H_2O by D_2O either the temperature has to be increased to *ca.* 130 K in order to observe the step in the same pressure regime, or that the pressure increases when the temperature is kept at 125 K. Neither of these effects seems to be observable in the study with D_2O HDA.[41] We conclude that it is important to know the accuracy of the temperature measurement in ref. 41, and whether the sample had warmed up for a short time to a higher temperature either before, or during the measurement lasting for *ca.* 10 h at 100 K. Klotz *et al.* further reported that in their experiment at 0.7 GPa and 100 K "HDA returns to its original density when decompressed at 80 K, whereas VHDA remains permanently densified".[41] This is even more surprising and it contradicts our findings,[7,32,80] those of other experimental groups,[38,77] and of simulations.[61,62,75] We note, however, that the molar density reported in ref. 41 for D_2O HDA does not allow to distinguish because recovered HDA and VHDA, with HDA and VHDA molar densities of 0.0650 and 0.0694 mol cm^{-3} (calculated from H_2O densities of 1.17 g cm^{-3} for HDA and 1.25 g cm^{-3} for VHDA), cannot be distinguished by the molar density value of 0.07 mol cm^{-3}.[41]
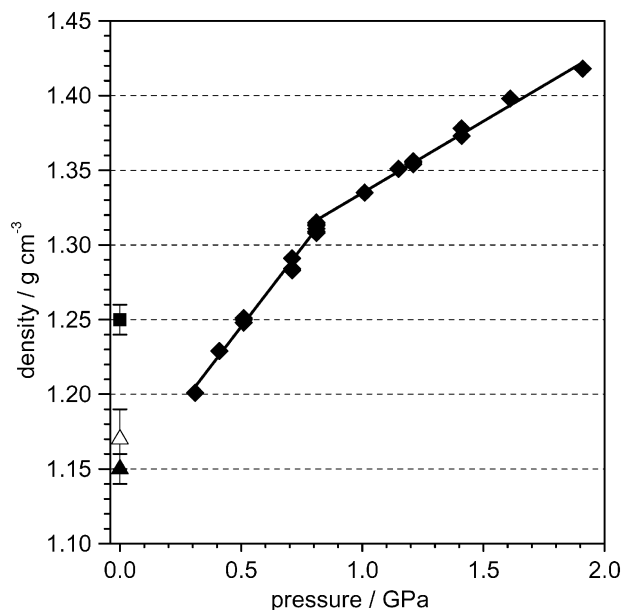

Fig. 6 Density values of relaxed amorphous ice calculated from the densities of crystalline high-pressure ices in the pressure range 0.3 to 1.9 GPa. Linear fits below and above 0.8 GPa (with correlation coefficients of 0.996 for each linear fit) are indicated by thick black lines with gradients of 0.21 g cm^{-3} GPa^{-1} below 0.8 GPa and 0.10 g cm^{-3} GPa^{-1} above 0.8 GPa. Density values of HDA and VHDA at 77 K and 1 bar from ref. 7 are depicted by a full triangle and a full square. Mishima *et al.*'s density value of HDA at 77 K and 1 bar is shown by an open triangle.[5] See ref. 32 for further details (from ref. 32 with changes.)

Thermodynamic phase transition or kinetic densification?

For the interpretation of the conversion from HDA to VHDA shown here there are basically two options: (a) a true thermodynamic phase transition, or (b) a kinetic densification process that takes place in a nonlinear, accelerating and decelerating, fashion, so that steps in density result. The slopes of the pressure–density curves at 125 K (bottom panel, Fig. 5) yield information on whether the compression process takes place elastically or inelastically. By elastic compression we mean that $d\rho/dp$ is constant within experimental error, whereas on inelastic compression it increases largely. Elastic densification of VHDA and HDA correspond to slopes of *ca.* 0.10 and *ca.* 0.14 g cm^{-3} GPa^{-1} (*cf.* ref. 80 for details). These values are very close to those observed in Fig. 5, bottom panel, between 0.55–0.80 GPa after the first densification step and at > 1.1 GPa after the second step. So we conclude that inelastic compression takes place only in the areas numbered 1 and 2 in Fig. 5. This finding has implications on the current debate on the relation between HDA and VHDA. Whereas Mishima infers a continuous crossover from the slope dp/dT of the melting/amorphization curves and argues "that the different HDA ices are all in the same HDA 'megabasin' on the potential-energy surface",[67] Debenedetti and Stanley, on the other hand, called this an open question by asking "whether VHDA is a distinct phase separated from HDA by a first-order transition or whether it is simply very dense HDA".[3,4]

Structurally, LDA, HDA and VHDA can be distinguished by the number of water molecules in the first coordination shell which increases from 4 to 5 and 6, respectively.[37,74] This implies that the number of interstitial water molecules has to increase by one molecule to produce HDA from LDA and by another molecule to produce VHDA from HDA. Since these two changes in structure are quite similar, it seems plausible that the LDA–HDA relation should be similar to the HDA–VHDA relation. The observation of two steps on isothermal compression seems to confirm this idea even if the second step is less sharp. Theoretical calculations on supercooled and amorphous water[59,63] as well as on model potentials[82] suggest that a thermodynamic transition between HDA and VHDA is possible by showing that several metastable liquids separated by first-order phase transitions and critical points can be found. However, there are also simulations suggesting rather a kinetic densification.[61,62,65,75]

We further discuss the relevance of Fig. 6, the density *versus* pressure plot, for the relation of HDA and VHDA. The abrupt change of slope at *ca.* 0.8 GPa could indicate indeed formation of a distinct phase. A first-order phase transition requires a discontinuity in density which does not seem to occur at first sight. A second-order phase transition, which requires a change of slope in the volume (density) *versus* pressure plot, could be compatible with Fig. 6. Second-order transitions in general are known to show dynamic density fluctuations at pressures (temperatures) below the critical pressure (temperature).[83] It is conceivable that the irreversible relaxation phenomena and densification observable in our Fig. 6 below *ca.* 0.8 GPa are an indication for dynamic density fluctuations of a second-order transition. However, within our experimental error it is not possible to discriminate between an abrupt and continuous and a discontinuous change of slope at *ca.* 0.8 GPa (see discussion in ref. 15). Thus, it is not possible to discriminate clearly between first-order and second-order phase transition and a continuous transformation.

In the debate on the relation between HDA and VHDA, Andersson's[72] recent study of pressure-amorphized ice I_h by dielectric relaxation spectroscopy becomes important. He found that VHDA relaxes in *ca.* 1 s at 140 K and 1 GPa and that relaxation is virtually unaffected by pressure. He summarizes that "VHDA at 1 GPa is in a metastable equilibrium state at temperatures above 140 K, *i.e.* an ultraviscous water state. This state would be achieved if water at 1 GPa could be supercooled through its ice VI phase boundary to *ca.* 140 K". If this holds true, it could be considered to be consistent with a thermodynamic HDA → VHDA phase transition, with VHDA being in a metastable ultraviscous state. Here it would be very important to know whether HDA can also be transformed into an ultraviscous liquid state. This could be done by determining HDA's relaxation on isobaric heating at a pressure where it converts neither to LDA nor to elastically compressed VHDA (*e.g.*, at 0.30 GPa, *cf.* Fig. 2 in ref. 32).

Concluding remarks

One of the main issues in the current debate on polyamorphism of water is how LDA, HDA and VHDA are related to each other. The future avenue may be the understanding of the behaviour of these amorphous forms and of glasses generally, under pressure.[30,31] Here we show that the relation between HDA and VHDA is similar to the relation between LDA and HDA. At 125 K a density step can be found both on compressing LDA above 0.40 GPa to HDA and on compressing HDA above 0.95 GPa to VHDA. These density steps may be kinetically driven or may imply a first-order like phase transition at elevated pressure. In agreement with this, a plot of the densities of HDA relaxed under pressure *versus* pressure shows both a linear regime below *ca.* 0.8 GPa and a linear regime with another gradient above *ca.* 0.8 GPa (Fig. 6). This implies that indeed a new phase may also form above *ca.* 0.80 GPa and *ca.* 160 K. However, we cannot distinguish within our experimental uncertainty whether there is a density jump at *ca.* 0.8 GPa between the two linear regimes, which is required for a first-order like phase transition, or whether the two linear regimes form a kink at 0.80 GPa, which indicates a second-order like phase transition, or whether the two linear regimes are connected in a continuous manner.

It is intriguing to think that the two steps between LDA, HDA and VHDA observed in ref. 80 are analogs in the glassy state for phase transitions between a low-, a high- and a very-high-density liquid. Our finding that at slow compression rates and 125 K the inelastic conversion from LDA to HDA (0.35–0.55 GPa) develops into elastic compression of HDA (0.55–0.80 GPa), then into inelastic conversion from HDA to VHDA (0.80–1.10 GPa) and finally to elastic compression of VHDA (> 1.10 GPa) points in the direction that densification of amorphous ice occurs as two thermodynamically distinct transitions. Nevertheless, we cannot presently exclude the

alternative option of a kinetically controlled densification process in amorphous ice that accelerates and decelerates in specific pressure ranges corresponding to the two lynch pin sites being filled with a first and second water molecule. What is missing, though, is to demonstrate experimentally reversibility of the HDA → VHDA transformation in the same manner shown by Mishima for the LDA → HDA transformation.[45]

A consequence of the existence of two distinct phase transitions between LDA and HDA and HDA and VHDA, would be that the liquid–liquid phase transition hypothesis[8] would have to be amended because in that case three distinct phases of glassy water do exist.[84] This could be done in line with recent simulations.[59,63,82,84]

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