PHYSICAL REVIEW B **76**, 134103 (2007)

In situ transformation of amorphous ices at high pressures

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(Received 18 June 2007; revised manuscript received 14 August 2007; published 4 October 2007)

By using thermal conductivity and its change with temperature and pressure as a criteria for *in situ* structural transformation of the crystalline and amorphous solid forms of water, we report two findings: (i) transformation of high-density amorph (HDA) directly to cubic ice on slow depressurization and (ii) slow transformation or dilation of metastable HDA at 130 K to a low-density amorph (LDA) even when the pressure was increased from 0.2 to 0.3 GPa, and then gradual reversion by collapse of the LDA to HDA on further pressurization to 0.5 GPa. We also discuss implications of these findings for the current understanding of the transformations of metastable ices under pressure, particularly of those studied *in situ*.

DOI: 10.1103/PhysRevB.76.134103 PACS number(s): 64.70.−p, 62.50.+p, 66.70.+f

I. INTRODUCTION

The energetic variability of hydrogen bonds is clearly evident from the fact that there is a multiplicity of amorphous solid states of water and of crystalline ices that are produced at different temperatures T and pressures p. When pressurized to $p > 1$ GPa at $T < 145$ K, hexagonal and cubic ice, ice I_h and I_c, convert irreversibly to a high-density amorphous structure generically called HDA.[1,2] The transformation of ice I_h to HDA occurs in a time-dependent,[2–4] pressure-dependent,[5] crystal-size-dependent,[6] and temperature-dependent[1,7,8] manner. It was proposed that increase in pressure collapses ice I_h to HDA instead of melting it.[9] The conclusion that "collapse of crystalline order and of hydrogen-bonded structure under a uniaxial stress is a more likely cause of the pressure-induced amorphization than is melting" was deduced from earlier studies in which an ice clathrate, whose melting point is much more sensitive to pressure than that of ice I_h, did not amorphize on compression in the same manner as ice I_h (Ref. 10) but ice I_c, which has shown no melting point, did amorphize under pressure.[11] The pressure-collapse mechanism has also been discussed in terms of a violation of Born stability conditions at high pressures that transforms one crystal form to another.[12] The use of the Born stability violation as a mechanism of amorphization of the ices and other solids at high pressures[9] has been critically discussed.[3]

The high-density amorphous structure, in turn, irreversibly transforms to a low-density amorph (LDA) when heated from ~77 K at a pressure $p < 0.07$ GPa,[2,13] or else depressurized quickly at a temperature T in the range of 120–140 K.[7,13,14] A low-density amorph similar to LDA is obtained apparently by depressurizing ice VII to ambient pressure at 77 K and then heating to $T > 120$ K,[15] and also by a similar treatment of ice VIII.[16] When these low-density amorphs are heated, they transform to ice I_c. Heating of high-pressure crystalline phases of ice at ambient pressure also produces ice I_c,[18] and this has been used as a method for producing ice I_c. It has been found from x-ray studies of recovered samples at ambient pressure that under certain conditions of heating and at high pressures in the range of 0.2–1.4 GPa, HDA transforms also to ices IV, V, VI, IX, and XII,[18] and to a mixture of ice I_h and ices V and IX.[18] The crystallized form recovered at ambient pressure depends on the heating rate and the pressure on HDA,[18] and in some cases even similar heating rates have produced different crystal phases.[18] The ices formed on spontaneous crystallization persist in metastable conditions as "intruder phases" in the p-T domain of stability of other ices, and they have been studied in those conditions. More relevantly, *in situ* neutron diffraction studies in the pressure range of 0.3–3.9 GPa (Ref. 19) have shown that when HDA at different pressures is heated to different temperatures, ices IV, V, VI, and XII and/or their mixtures are produced, and on isothermal compression HDA at 100 K crystallizes to an ice-VII-like structure at 2.5 GPa.[19] However, as in a (nonequilibrium) transformation that involves at least one metastable phase, the p-T conditions for the formation of the crystalline ices have remained irreproducible. This suggests that the recovered form and its formation at high pressures are determined by competition in the crystal growth rates. Although attempts have been made to provide conditions for the formation of the ices, transformations of HDA to different crystal phases appear probabilistic. To explain that, it had been suggested[6] that HDA may be a mixture of various nanometer-size high-pressure crystalline phases in a thermoelastic equilibrium,[20] and not vitreous. (A thermoelastic equilibrium refers to the condition in which two crystal phases coexist when the Gibbs energy decrease on the phase transformation is opposed by the elastic energy increase at the two-phase interface. Slow diffusion of point defects into the interface may decrease the elastic energy, and thus further crystal growth can occur.[21,22])

Because of the importance of the role of solid forms of water in several scientific and technological disciplines, there is a general interest in understanding the properties of its amorphous forms and the p-T conditions of their metastable existence. A phase diagram based on the free energy estimates of LDA and HDA assuming the two to be in a thermodynamic equilibrium has been constructed,[23] and the two-step densification on pressurization of LDA to the so-called very high-density amorph (VHDA) or ultimate dense form has been studied as part of amorphous-amorphous transitions.[5] The gradual transformation from LDA to HDA and VHDA has been explained by molecular dynamics and other simulations.[24,25] Diffraction studies have concluded that continuous transformation to denser amorphs occurs when water molecules are forced in a position beyond the first order coordination shell.[26–28] Structural characterization of VHDA has led to the revision of the conjecture that high-density and low-density liquid water may coexist at certain p-T conditions.[29] High resolution inelastic x-ray scattering of both HDA[30] and LDA[31] have shown that despite the structural disorder, their dynamic response appears crystal-like, and thermal conductivity studies have shown that although LDA shows a crystal-like dependence of thermal conductivity on temperature, HDA does not.[13] Two recent articles have reviewed most of the experimental studies[32,33] and computer simulation[33] of the transformations. Since then, neutron scattering experiments have shown that HDA does not constitute any particular form of water's hydrogen-bonded network,[34] and *in situ* Raman spectra studies[35] have found that in one case, decompression of HDA produced a low-density amorph distinct from LDA. Raman spectra measured during the annealing of the collapsed ice I_h at 0.1 MPa have shown[36] that its profile changes continuously as the volume increases irreversibly. The LDA produced by collapsing ice I_h at 77 K and ~1.2 GPa, heating it to 150 K at 1.5 GPa, recovering at 77 K at 0.1 MPa, and then finally slow heating has shown that when annealed in the T range of 120–140 K at 0.1 MPa, it transforms to a hydrogen-bonded structure whose OH-stretching vibrational region irreversibly shifts to lower frequencies, a feature not observed for glassy water or amorphous solid water.[37] This also suggests a multiplicity of structures for the solid generically referred to as LDA. We also point out that despite the same density in the T range of 25–145 K, the OH-stretching vibration peak of LDA in the ~3100 cm^{-1} range is ~25 cm^{-1} higher than that of ice I_c.

However, most research has been performed on samples recovered at ambient pressure, which causes uncertainty in the interpretation of the transformations, as is known from the finding that the high-pressure ices recovered at ambient pressure, in their metastable state, transform on heating to ice I_c.[17] Such ambient pressure studies of LDA and HDA also overlook the consequences of elastic expansion of the samples on decompression. While it is recognized that *in situ* studies at high pressures are needed to understand the nature of the transformation, such studies are rare. Yoshimura *et al.*[35] have summarized some of the studies on LDA and HDA, and Johari and Andersson[32] have provided a review of the vibrational and relaxational properties measured during their *in situ* transformation. However, even the *in situ* studies of the high-density and low-density amorphs do not indicate that the same state of each solid is formed because the method of production by the pressure collapse of ices I_h and I_c differ. Briefly, it has been found[3] that different states of the so-called VHDA are also produced by extremely slow pressurization of ices I_h and I_c at $T \geqslant 130$ K by a time- and temperature-dependent transformation, whose kinetics has been studied. Irreversible transformation of HDA to LDA at ambient pressure is also time dependent. Its kinetics has been studied at different T,[38,39] and it has been concluded that the different intermediate structures formed at ambient pressure are strongly heterogeneous on a length scale of several nanometers.[40] Studies of x-ray scattering and molecular dynamics simulations of annealing of VHDA have shown a continuous emergence of a new network, which is very different from the presumed classic first order transition.[41] It has also been suggested that intermediate phases formed during the HDA to LDA transformation at ambient pressure are not equilibrium mixtures of HDA and LDA,[42] and the nature of this transformation observed *in situ*[43] has been debated.[44,45]

Here, we report two findings: (i) *in situ* transformation of HDA produced by slow pressurizing directly to ice I_c on slow depressurizing, an occurrence that seems to be kinetically preferred in the presence of ice I_c or another crystalline ice, and (ii) possible slow transformation of this metastable HDA to LDA on slow pressurizing in the presence of ice I_c and probably another crystalline phase, an occurrence that seems opposite of what has been observed in earlier studies. It should be pointed out that thermal conductivity κ on pressure amorphization of ices I_h and I_c decreases by a factor of 5,[13] and the volume only by at most 40%.[1,5] Since κ is much more sensitive to the transformation than the volume and is therefore a better indicator of the transformation, we use its measurements to follow the *in situ* transformations of the water's amorphs at high pressures. Also, *in situ* diffraction and spectroscopy measurements have used millimeter-size or smaller samples, and their κ cannot be measured simultaneously. We further consider the implication of these findings for our current understanding of phase transformation of the crystalline and amorphous solid water in metastable states.

II. EXPERIMENTAL METHODS

The hot-wire method was used to measure the thermal conductivity κ of the crystalline and amorphous solid states of water. It has been described in detail earlier.[46–48] Briefly, the method is based on a mathematical solution of the time-dependent equation for heat conduction.[49] In this solution, the temperature rise ΔT of an infinitely long, infinitely conducting wire immersed in an infinitely large specimen is[49]

$$\Delta T = \frac{2q\alpha^2}{\pi^3\kappa} \times \int_0^\infty \frac{1-\exp(-\beta u^2)}{u^3\{[uJ_0(u)-\alpha J_1(u)]^2+[uY_0(u)-\alpha Y_1(u)]^2\}}du, \tag{1}$$

where q is the constant heating power input per unit length, $\alpha = 2\rho C_p/(\rho_w C_w)$, $\beta = \kappa t/(\rho C_p r^2)$, t is the time, r is the radius of the hot wire, ρ and C_p are the density and heat capacity of the specimen, ρ_w and C_w are the density and heat capacity of the hot wire, J_0 and J_1 are Bessel functions of the first kind of zero and first order, and Y_0 and Y_1 are Bessel functions of the second kind of zero and first order.

The hot-wire sample cell was a ~30 mm deep and 37 mm internal diameter Teflon container with a tightly sealing Teflon cover. The Teflon cell is closely fitted inside in a piston-cylinder type of apparatus of 45 mm internal diameter, and the whole assembly is transferred to a hydraulic press that supplies the load. Temperature is varied by heating or cooling the whole vessel. The latter is done via a built-in refrigerator, which uses a closed helium gas cycle.[50] The advantage of using a built-in refrigerator is that the friction between the piston and vessel is greatly reduced since it is placed in vacuum, which precludes frost formation. Moreover, the temperature can be kept constant to within ~1 K by a controller. The temperature is measured by a chromel-alumel thermocouple, which has been calibrated against a commercially available silicone diode thermometer. Pressure is determined from the load/area with an empirical correction for friction, which has been established through an *in situ* experiment using the pressure dependence of the resistance of a manganin wire. The hot wire itself was a 0.1 mm diameter, 40 mm long Ni wire. In order to best use the limited space available in high-pressure equipment, the wire was placed horizontally in a ring of constant radius within the Teflon cell. At each heating event, the hot-wire probe, which is surrounded by solid water is heated by a 1.4 s long pulse of nominally constant power during which the wire resistance was measured as a function of time. The wire acted as both the heater and the sensor for the temperature rise, which was calculated by using the relation between its resistance and temperature. Equation (1) for the temperature rise with time was fitted to the data points for the hot-wire temperature rise, thereby yielding κ. The inaccuracy in κ thus measured was ±2% at 298 K. As the temperature coefficient of the electrical resistance of the nickel hot wire decreases with the decrease in the temperature, the inaccuracy of the measured κ value increases to about ±4% at 40 K. The standard deviation of the data obtained in these measurements is an order of magnitude smaller than the inaccuracy. The actual pressure on the sample was determined from calibration for the pressure-increase part of the cycle when friction between the moving components caused the actual pressure to be less than the measured value. For the pressure-decrease part of the cycle, the actual pressure was estimated by assuming that the friction in the assembly is symmetric in a pressure cycle. Thus, the reversed friction (pressure) was added to the measured pressure.

III. RESULTS

The measured κ of the crystalline ices used and amorphous ices formed on pressurization is plotted against the pressure p in Fig. 1. A sample of ice I_h was made in the Teflon cell by freezing water, and the sample was cooled to 130 K. It was then pressurized at a rate of ~0.1 GPa/h up to the onset of amorphization at which pressure the rate was lowered to ~0.05 GPa/h. The plot of κ against T shows the onset of amorphization at ~0.8 GPa by an inverted sigmoid shape decrease in κ.[13] This decrease is qualitatively similar to the decrease in the volume observed at higher pressures for ice I_h at 77 K, but, quantitatively, the decrease in κ is by a factor of 5 while that in volume is by ~40%.[1] The slight vertical discontinuities of the plot at p near 1 GPa and at 1.1 GPa along the path 1→2 are due to the fact that the pressurizing was stopped from increasing for a certain time period at these p, and during this period the sample's κ decreased at a fixed p and T with time, an observation already discussed in detail.[2–4] During the course of transformation at 130 K, κ decreased from ~3.3 W m^{-1} K^{-1} at the onset of amorphization to 0.68 W m^{-1} K^{-1} at 1.25 GPa.

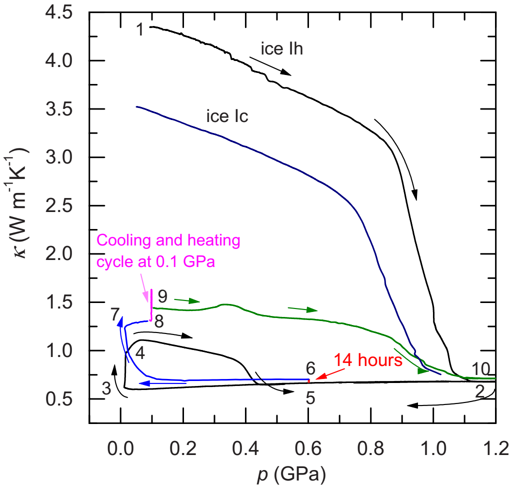

FIG. 1. (Color online) Changes in the thermal conductivity on the transformation of ice I_h and ice I_c to HDA on pressurizing at about 130 K and to LDA, ice I_c, and other phases on pressurizing-depressurizing cycle at about 130 K. The paths denoted by numbers and the reversible and irreversible changes are described in the text. [Ice I_c was made by heating ice II (Ref. 17), which, in turn, was produced by pressurizing ice I_h at ~225 K to 0.25 GPa. Ice II at 0.25 GPa was subsequently cooled to 175 K, the pressure released slowly to 0.05 GPa and the temperature decreased to 145 K. The sample was then heated from 145 to 185 K at 0.05 GPa. It showed a transformation to ice I_c with an onset at about 170 K. Ice I_c was then cooled to 130 K, and the sample was pressurized isothermally.]

The HDA sample thus formed was then depressurized at a rate of 0.15 GPa/h to 0.75 GPa and then kept for 9 h (during the night) at 0.75 GPa at 130 K, during which its κ increased by 0.3%, which is within the imprecision of the method. Subsequently, the pressure was lowered isothermally to ~0.03 GPa (point 3) at the 0.15 GPa/h rate, where κ increased *abruptly* with a slight simultaneous pressure increase (point 4), which shows that a rapid transformation to a bulkier phase had occurred. The pressure was then immediately increased at the 0.2 GPa/h rate and κ showed a broad sigmoid shape decrease beginning at ~0.35 GPa, and at 0.45 GPa its κ became equal to the value measured during depressurization of HDA.[13] Further increase in p up to point 5 increased κ slowly along the same path as 2→3. This constitutes one irreversible cycle of measurements: 2→3→4→5. On the basis of earlier findings, path 1→2 is for the irreversible collapse of ice I_h to HDA, path 2→3 is reversible for the pressure dependence of κ of HDA, path 3→4 is for the irreversible conversion of HDA to LDA, and path 4→5 is for the irreversible conversion of LDA to HDA.

It should be stressed that the sample studied here was produced by very slowly pressurizing ice I_h and ice I_c at 130 K and taking ~15 h to reach 1.2 GPa. This is in contrast to the HDA made by rapidly pressurizing ices I_h and I_c at 77 K to 1.5 GPa in a few minutes. Since the pressure collapse is found to be both pressure and time dependent[1–5,7,8] and reaches completion more quickly at high temperatures than at low temperatures, the amorph produced by slow pressurization of ices I_h and I_c at 130 K over a period of ~15 h in our study is likely to be the ultimate state of the high-density amorph. This aspect is to be particularly noted because there is a confusion regarding the identity of various "HDAs" that had been produced by pressurizing ice I_h at different temperatures to different pressures over a relatively short and often unspecified time period.[1,8] Moreover, an ultimate, presumably highest density HDA seems to have been produced when the amorphous solid formed by pressurizing ice I_h at 77 K was heated to 160 K while under pressures greater than 0.8 GPa.[51,52] More recently, pressurization of HDA at 125 K at the slowest rate of 1.2 GPa/h has shown an irreversible sigmoid shape increase in the density in the pressurization range of 0.8–1 GPa, which has been attributed to the transformation of HDA to VHDA.[5,53] Since the temperature in our study is 5 K higher and the pressurization rate is at least 12 times to 24 times slower, the sample studied here would be VHDA in their terminology, as discussed earlier;[32] i.e., its density would be closest to that of the ultimate dense state produced by the collapse of ices I_h and I_c. Since there is a gradation of density and structure of the high-density amorphous ices, we have referred to our samples as simply HDA to avoid confusion while maintaining that it differs from the HDA produced by relatively fast pressurizing at 77 K.[1,8] Subsequently, the sample was kept at 0.6 GPa and at around 130 K during 14 h. This caused κ to increase by 5.4% simultaneously as the temperature drifted up to 5 K (5 to 6). As κ of HDA varies as $\kappa \sim T^{0.026}$ at 0.1 GPa and as $\kappa \sim T^{0.2}$ at 1 GPa,[47] the temperature drift can only account for a maximum of 0.8% increase in κ. It follows that the main part of the increase must be due to the slow growth of a crystalline phase, which changed the transformation behavior during the following pressure cycle: $6 \to 7 \to (8 \to 9) \to 10$. The sample was first depressurized at 0.2 GPa/h (path $6 \to 7$) during which its κ began to *slowly* increase at ~0.1 GPa and reached 1.25 W m^{-1} K^{-1} at point 7 at p of ~0.03 GPa. The sample was then pressurized at 0.2 GPa/h to 0.1 GPa (point 8), cooled to 95 K, and then heated to ~130 K at 0.1 GPa ($\kappa \sim T^{-0.4}$ below 125 K, where the data on heating retraced the data on cooling, showing that the sluggish transformation had become very slow) during which its κ at 130 K had increased from 1.3 W m^{-1} K^{-1} before the cooling to 1.43 W m^{-1} K^{-1} after (point 9). It was then pressurized at 0.15 GPa/h. As seen in Fig. 1, its κ first increased and then decreased, thus producing a broad peak in the 0.2–0.45 GPa range. Thereafter, κ decreased in a sigmoid shape manner to 0.71 W m^{-1} K^{-1} at 1.25 GPa and 130 K, as shown by the path $9 \to 10$. At 1.25 GPa (point 10), κ is 5% higher than at point 2. Thus, the p-T cycle, $2 \to 5 \to 6 \to 7 \to 8 \to 9 \to 10$, did not restore the original κ value, and the difference corresponds to that produced during the slow increase in κ at 0.6 GPa (5 to 6). The path $2 \to 5 \to 2$ is cyclical. If only one form of HDA persists, the path between 2 and 3 would be reversible. This indicates that change in the state of the high-density amorph formed on slow pressurization, if any, is undetectable on pressure cycling in the (more sensitive) κ measurements.

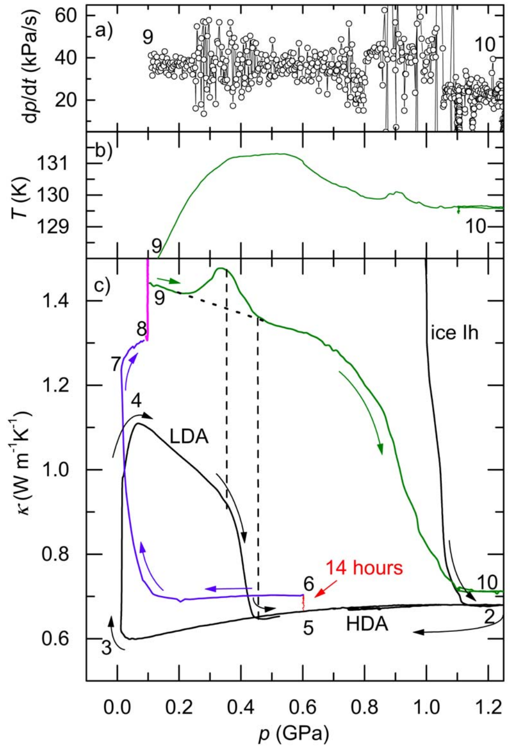

FIG. 2. (Color online) (a) Time derivative of the pressure reading during pressurization of a mixture of initially mainly ice I_c and HDA, as described in the text. (b) Temperature during pressurization of a mixture of initially mainly ice I_c and HDA. (c) Changes in the thermal conductivity on the transformation of HDA on depressurizing, transformation to LDA on depressurizing, and then back to HDA on pressurizing shown by the path $2 \to 3 \to 4 \to 5 \to 2$. Also shown are the depressurizing and pressurizing conditions that appear to convert HDA to LDA, while coexisting with ice I_c, and then back to HDA on pressurizing, hence the appearance of a peak in thermal conductivity. The vertical dashed lines indicate the LDA to HDA transition range, and the dotted line indicates the thermal conductivity as a function of pressure for the initial composition at point 9. Details are given in the text. The plots are redrawn from the data in Fig. 1.

IV. DISCUSSION

For convenience of discussion, we have redrawn details of Fig. 1 here in Fig. 2(c) and have included plots of the time derivative of the p reading and T of the sample measured simultaneously with k against p [Figs. 2(a) and 2(b)], with the labeling remaining the same as in Fig. 1. In the cycle $2 \to 3 \to 4 \to 5 \to 2$, the findings are consistent with earlier studies that have shown that HDA at 130–140 K transforms to LDA at a nominal pressure of 0.05 GPa on depressurizing and LDA transforms to HDA at ~0.3 GPa on subsequent pressurizing.[7] It also shows that while $(d\kappa/dp)_T$ is positive for HDA, it is negative for LDA.[13] In contrast, the pressure derivative of volume for both HDA and LDA is negative as for materials generally.

The transformation behavior in the second cycle is more complex. In Fig. 2(c), κ of the mixture of ice I_c obtained via path $2 \to 5 \to 6 \to 7 \to 8 \to 9$ is 1.44 W m^{-1} K^{-1} at 129 K and the lowest pressure of 0.1 GPa and, like the crystalline ices I_c and I_h and LDA, $(d\kappa/dp)_T$ is negative. The corresponding κ for pure ice I_c in Fig. 1 is 3.5 W m^{-1} K^{-1}.[13] The lower κ value of the mixture shows that it contains a significant amount of HDA and possibly LDA and small amounts of a high-pressure crystalline phase that had formed in the path $5\rightarrow6$. The latter is based on the difference that appears between the value for κ of the sample in the beginning and that at the end of the complete cycle $(2\rightarrow10)$, which is 5%. Thus, the crystals that formed in the path $5\rightarrow6$ and increased κ by 5% remained during the rest of the cycle. These crystals would be those of one of the crystalline ices which do not show pressure-induced amorphization at ~1 GPa. Moreover, in the paths $2\rightarrow5\rightarrow6\rightarrow7\rightarrow8\rightarrow9$, there is no indication of an *abrupt* transformation of HDA to LDA on depressurizing the sample from 0.6 GPa at 130 K. This means that the sample contains a significant amount of mostly HDA and ice I_c at 130 K and 0.1 GPa. When the sample is pressurized from point 9, κ begins to increase from 1.42 W/m^{-1} K^{-1} at ~0.2 GPa to 1.48W/m^{-1} K^{-1} at 0.32 GPa. Thereafter, it decreases on further pressurizing to 1.35 W/m^{-1} K^{-1} at 0.49 GPa, thus showing a broad peak in the κ-T plot. This peak is centered at ~0.34 GPa. As shown by the dotted line, the κ value before this peak at 0.2 GPa linearly extrapolates to the κ measured at ~0.45 GPa after the peak. In Fig. 2(b), T also continuously increases from 128 to 131 K as p is increased from 0.1 to 0.5 GPa. In relevance to the appearance of the κ peak on pressurizing from 0.1 to 0.3 GPa, the sample's temperature gradually increases from 128 to 131 K, and after the peak has appeared it decreases to ~130 K at 0.8 GPa [Fig. 2(b)]. The gradual increase in T with increase in p is due to heating from low T at 0.1 GPa, and not due to an exothermic effect. Since κ of this (mixed phase) sample decreases with increase in T $(\kappa \sim T^{-0.4})$ and p, the increase in T by ~3 K or more would not increase κ of the mixed sample and would therefore not account for the rise of κ to a local peak value in Fig. 2(c).

Along the path $5\rightarrow6\rightarrow7\rightarrow8\rightarrow9\rightarrow10$, a total of five irreversible transformations may occur: (i) transformation of HDA to an unknown high-pressure crystalline ice $(5\rightarrow6)$, (ii) transformation of HDA to ice I_c $(7\rightarrow8\rightarrow9)$, and (iii), (iv), and (v) all in the path $9\rightarrow10$, transformations from HDA→LDA, LDA→HDA, and ice I_c to HDAs, respectively. Ultimately, the high-pressure crystalline phase persists with HDA at state point 10. At points 7 and 8 in Fig. 2(c), the sample contains ice I_c, HDA, and an unknown high-pressure crystalline ice formed in the path $5\rightarrow6\rightarrow7\rightarrow8$. Its κ is higher than that of LDA at point 4, predominantly because of ice I_c. From $8\rightarrow9$, some of the HDA transforms to ice I_c, and possibly also a slight amount of HDA transforms to LDA; further pressurizing from point 9 decreases κ of both ice I_c and any LDA present. The rate of decrease, $d\kappa/dp$, of the mixture is less than that for both ice I_c and LDA because it is partly compensated by the positive $d\kappa/dp$ for HDA in the mixture.

Therefore, the increase in κ, leading to a local peak at 0.34 GPa in Fig. 2(c), would indicate that ice I_c and/or HDA in the mixed sample transform/s to another ice phase whose κ is higher than both of ice I_c and HDA. The decrease in κ and its return to the original value thereafter indicates reversion of that ice phase to the original ice I_c and/or HDA at a higher pressure. However, studies of the change in volume[7] and κ (Ref. 13) have shown that when ice I_c at 77 K$<T<$130 K is pressurized, it does not transform to another crystalline ice. Instead, it begins to collapse to HDA at 0.7 GPa. This collapse process is time dependent, as described in our interpretation[2] of the vertical decrease in volume at a fixed pressure observed by Floriano *et al.*[54] It is also temperature dependent, as the onset pressure has been found to be 0.9 GPa at 77 K,[55] ~0.94 GPa (0.99 GPa−0.05 GPa for hysteresis) at 77 K (Ref. 54) and 0.6 GPa at 145 K.[7] (A similar time and temperature dependence of the onset pressure has been found also for ice I_h.[3,4]) Although our discussion is necessarily limited to *in situ* transformations, it should be noted that, at ambient pressure, the pressure-collapsed ice I_c (HDA made from ice I_c) has been found to differ slightly in structure and enthalpy, and significantly in crystallization kinetics, from the pressure collapsed ice I_h (HDA made from ice I_h) under identical p-T conditions.[56] Moreover, the study[56] has indicated that the LDA formed by heating HDA from ice I_c at ambient pressure differs from the LDA formed by heating HDA from ice I_h, thus suggesting that the material known as LDA also has different states.

Moreover, when HDA at 77 K is pressurized or depressurized in the range 0.01–1.5 GPa, it does not transform to another phase.[1] But when HDA at 120–140 K is pressure cycled in the same range, it transforms apparently reversibly to LDA,[5,7,13,14] but the pressure for the HDA→LDA transformation differs from that for the LDA→HDA transformation by as much as ~0.3 GPa. Therefore, the increase in κ on the left side of the broad peak seen in Fig. 2(c) may be due to the transformation of HDA to ice I_c or LDA, but not of HDA to VHDA because HDA at p of ~0.8 GPa transforms to VHDA on heating at a fixed rate from 77 to 160 K,[51] or near 0.9 GPa during isothermal pressurization at 125 K.[5] However, the subsequent decrease in κ indicates that further increase in p reverses the transformation, and this would not occur had ice I_c formed.

One may argue that the sample of ice I_c and HDA in this study may contain a small amount of a high-pressure crystalline ice that itself may have formed at 0.6 GPa (path $5\rightarrow6$) and persisted at 0.2 GPa and ~130 K, and this crystalline ice finally transformed to LDA at the onset pressure of the broad peak. If this was to occur, κ of the high-pressure crystalline ice would have to be less than that of LDA in order for κ to increase on transformation. To investigate further, we examine the κ value of other ice phases. Its variation with p is shown by the curves in Fig. 3, where the data taken from previous investigations[57–63] are compiled. The plots show that all of crystalline ice phases have a higher κ than LDA, and only HDA and ice clathrates have lower κ than LDA. Because of the higher κ value of crystalline ices, there is no possibility that a crystalline ice present with HDA may, by transforming to LDA on pressurization, increase the sample's κ to the peak value. One may also argue that this crystalline ice phase may transform to ice I_h or I_c whose κ is higher, which on further pressurization may transform to LDA, and the consequent decrease in κ may cause the peak to appear. But earlier studies have shown no direct transformation of the ices to LDA.

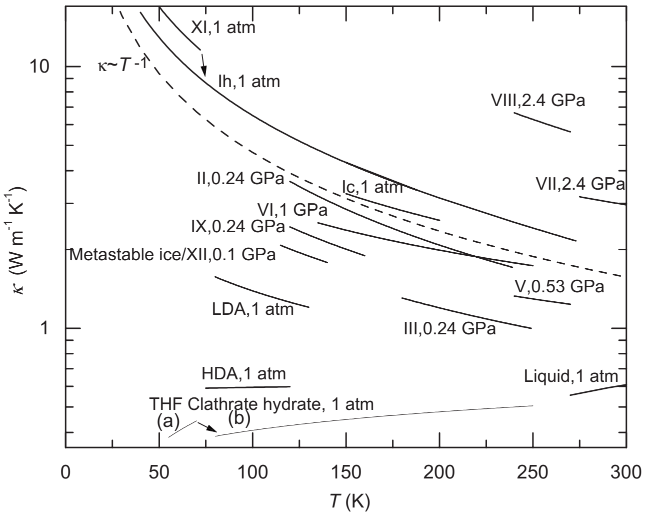

FIG. 3. The thermal conductivity of most of the crystalline ices, the ice clathrate containing tetrahydrofuran as guest molecules in the (a) ordered and (b) disordered states, and two amorphous solid phases of water is plotted against the temperature. The crystalline and amorphous ices and the pressure at which measurements were made are as indicated. Data are taken from Refs. 13 and 57–63.

The above-given elimination leaves us with the probability that metastable HDA in the sample at 130 K begins to transform by dilation to LDA in a time- and pressure-dependent manner. At a fixed (ambient) pressure of 0.1 MPa, metastable HDA transforms to LDA on heating at $T < 130$ K.[6,8,54,64] The irreversible process is kinetically controlled, and its rate increases with increase in T.[38] Also, in differential thermal analysis experiments performed at a fixed p, first up to 0.1 GPa and then up to ~1.1 GPa (arrows in Fig. 3 in Ref. 7), the onset temperature of this transformation increases. On depressurizing at T of ~130–140 K, HDA irreversibly transforms to LDA at ~0.06 GPa (Fig. 2, Ref. 7). The kinetics of this transformation has not been studied in detail at $p > 0.1$ MPa, but in one of our studies we found that on slow depressurizing isothermally at 130 K, HDA transforms to LDA in a few minutes at $p < 0.05$ GPa. The HDA's slow transformation to LDA likely begins at a lower p, but it becomes experimentally evident only at ~0.21 GPa and 130 K. (Isobaric slow heating, ~0.1 K min^{-1}, at $p > 0.05$ GPa also transforms HDA directly to ice I_c,[2] which further suggests that the thermal history of the sample and the structural state of the generic HDA partly determine the transformation's product.) The transformation continues when the sample is pressurized, and as its T increases slowly, its κ increases in this range, as seen in Fig. 2(c). At the κ-peak pressure of ~0.34 GPa, the transformation either becomes too slow or finishes, and in the now LDA-HDA mixture at 130 K, LDA does not begin to collapse to HDA until p of ~0.35 GPa is reached. An increase in p to ~0.45 GPa collapses more LDA and decreases κ to a value that lies on a line extrapolated (dotted) from $p < 0.21$ GPa in Fig. 2. This demonstrates that the sample's original composition at $p < 0.21$ GPa is restored on pressurizing to 0.45 GPa. More importantly, the recovery of κ to the extrapolated value at 0.45 GPa shows that the extent of transformation at ~0.21 GPa was insignificant. The LDA to HDA transformation range is shown by vertical dashed lines in Fig. 2. From mainly dilatometric studies at a fixed T of ~135 K, it has been deduced that HDA transforms apparently reversibly to LDA at ~0.2 GPa,[7] but with some hysteresis, and as T is decreased, this p increases.

It may seem counterintuitive that once transformation has begun, HDA would continue to dilate or transform to LDA on pressurization. Nevertheless, any transformation sequence such as phase I → phase II → phase I, which ultimately produces the original phase as indicated here by the restored value of κ, would most likely involve one transition to a bulkier phase. (Since we have measured κ and not the volume, one may argue that HDA could have transformed to one of the crystalline ices of about the same density but higher κ, such as ices III and IX. However, since ices III and IX do not transform to LDA on pressurizing, it is unlikely that the approach of κ to a peak value indicates transformation to a crystalline ice of the same density.) Also, since a *continued* transition to a bulkier phase on pressurizing, HDA to LDA here, may appear to violate the Le Chatelier principle obeyed by the reversible transitions, we point out that for metastable phases undergoing irreversible transformation, this principle would not be obeyed. Hence, the equilibrium thermodynamic relations may not apply for the effect of pressure on the HDA-LDA transformation. For example, metastable glasses or ultraviscous liquids crystallize slowly and irreversibly to a denser phase (exothermally) during heating, and this crystallization occurs over a temperature range far below their equilibrium freezing point. The pressure analog of this occurrence would be the continuation of an irreversible transformation to a stable bulkier phase on increasing the pressure at a slow fixed rate while the sample temperature is slowly increasing. The process is reminiscent of the freezing of (metastable) supercooled water to (bulkier) ice I_h on slow pressurizing and then melting of the ice I_h at the ice I_h–water phase boundary on further pressurizing, except for the fact that the freezing of supercooled water is explosive, and dilation of HDA to LDA and then collapse of LDA to HDA are slow, pressure-dependent processes.

We now consider the pV energy change in our experiments. The slow transformation of HDA to LDA occurring at a fixed p and volume increase ΔV would increase the energy of the sample by an amount of $p\Delta V$, and that occurring at a fixed V would increase energy by an amount of Vdp. In our experiment at an almost fixed volume, the pressure in the sample itself was not measured. Only the oil pressure that pushed the piston in the piston-cylinder assembly containing the sample was measured. Therefore, any increase in the sample's pressure dp would be superimposed on the instrument-controlled rate of increase of the oil pressure, and one may expect to observe a pressure increase. Since the pressurizing dp/dt rate is extremely slow, the HDA to LDA transformation itself occurs over a period of 0.8 h; the resulting force on the piston owing to the transformation to a bulkier phase is not likely to exceed the frictional force in the assembly. (Note that either a fraction of the total amount of HDA to LDA transforms at any pressure, so that the two coexist, or all the HDAs transform to an intermediate structure of LDA consequent to a continuous change in the short-range order.) Consequently, any rise in the pressure of the sample has remained undetected and the actual pressure on the sample is slightly higher than that measured from the oil pressure. Nevertheless, a small perturbation in the controlled increase in the oil pressure would be notable. For this reason, we examine the dp/dt of the pressure in the 0.21–0.32 GPa range, where the peak is observed. Its value is plotted against pressure in Fig. 2(a). The data show considerable random scatter in dp/dt in the pressure range where a κ peak in Fig. 2(c) is observed. We conclude that the extremely slow pV energy increase of the sample on the HDA to LDA transformation was not detected during the increase in p in our measurement assembly.

We also consider the thermodynamic aspects of the transition between the water's amorphs. It is known that thermodynamic and statistical mechanical treatments can never involve time as a variable, and for that reason any process that is time dependent may not be treatable in thermodynamic terms. However, the equilibrium state achieved at a virtually infinite time may be thermodynamically treatable. In this sense, transformations showing time-dependent hysteresis in the temperature or pressure are often difficult to interpret in thermodynamic terms unless it is ascertained that the midpoint condition of the hysteresis would correspond to an equilibrium condition. Nevertheless, on the basis that the free energy of LDA and HDA can be estimated from experimental data, their ΔG-p-T conditions have been determined and the phase boundaries and phase diagram constructed[23] by using the LDA-HDA equilibrium pressure of 0.2 GPa deduced by Mishima.[7] Also, the free energy ΔG against p plots have been estimated in Fig. 2 of Ref. 65 by fixing this equilibrium pressure, but it has been later shown[66] that the density and ultrasonic velocity of HDA made by pressurizing ice I_h are different from those of HDA made by pressurizing LDA. Also, the density and ultrasonic velocity of HDA depend on the p-T path used to make it from ice I_h. Thus, the properties of HDA and of LDA at a given p-T condition are path dependent, a conclusion that is further confirmed by the finding that identical pressurizations of ices I_c and I_h produce different HDAs.[56] This seems inconsistent with a thermodynamic description of the HDA-LDA phase equilibrium.

Moreover, the data for the construction of phase boundaries and phase diagram in ΔG-p-T dimensions[23] have been obtained from experiments in which ices I_h and I_c have been pressurized at a rapid rate. Since the densities of the amorphs thus produced were likely to be somewhat less than the density of the amorph produced by using very slow pressurizing rate in this study, it is not certain whether those ΔG-p-T estimates would be valid for the analysis of our findings. One may argue that the equilibrium conditions for the transformation are known since HDA and LDA have been found to coexist and to reversibly transform on pressure cycling.[35] However, this coexistence occurs over a much wider pressure range, thereby indicating a considerable uncertainty in the transformation conditions, and the transformation itself is *time dependent*.[14]

We now discuss the recent findings on the HDA → LDA → HDA transformations. Even with the different density and structure of the pressure-amorphized ices, their transformation to LDA at 130–140 K has shown a broad hysteresis in pressure, as much as 0.3 GPa when volume was measured.[7] In an *in situ* Raman spectroscopic study, Yoshimura *et al.*[35] found a much higher pressure range, 0.8–0.9 GPa, for the LDA to HDA transformation and did not find the transformation from HDA to LDA at the same pressure on decompression, as in Mishima's study.[7] In Fig. 3 of the study of Yoshimura *et al.*,[35] when a sample of HDA at 0.6 GPa was heated from 80 to 145 K, its Raman spectra showed an increase in the intensity of the 3500 cm^{-1} band. When the sample at 145 K was thereafter depressurized to 0.1 GPa, this band's intensity decreased, and it became indistinct. Concurrently, a band at 3150 cm^{-1} appeared. On pressurizing thereafter to 0.4 GPa, the original Raman spectra were recovered. Thus, the HDA sample at 0.4 GPa completely transformed to another phase on depressurizing to $p = 0.1$ GPa and then completely transformed back to HDA on repressurizing at $p = 0.4$ GPa. Thus, they showed[35] that HDA and another presumably low-density phase coexist and that the transformation is reversible; i.e., once the transformation has begun at 145 K, changing the pressure in the opposite direction reverses the direction of the transformation. Further analysis of the broad band feature appearing at 145 K and 0.6 GPa on heating at 0.6 GPa (Fig. 3, Ref. 35) suggested that the phase formed was distinct from the LDA of the earlier studies, which has been associated with the known LDA-HDA transformation. Thus, the *in situ* Raman spectra studies showed that the phases formed at 145 K (path 4 in Fig. 3, Ref. 35) differ from those formed at 140 K in path 4′ (Figs. 5 and 1 of Ref. 35). In an earlier study of LDA, formed by decreasing the pressure of ice VII′ at 135 K, LDA transformed to HDA around 0.3 GPa at a subsequent pressure increase,[67] which agrees with Mishima's result in the range 130–140 K.[7]

In the second set of our study, kinetically metastable HDA in the mixture with ice I_c begins to transform to LDA at a slow rate, and this rate becomes even slower as the sample is pressurized. The broad κ peak in Fig. 2 for our samples, which are close to the VHDA structure, appears when the state point has reached the equilibrium line for LDA. Our data indicate that this HDA transforms to LDA in the range 0.21–0.32 GPa at 130 K. Therefore, the midpoint pressure of a hysteresis loop for this HDA-LDA transformation is higher than ~0.32 GPa. The transformation of LDA to HDA occurs here in the 0.38–0.43 GPa range, as defined by the intersection points between the tangent line at the maximum transformation rate and the base lines before and after the transformation range. This transformation range is somewhat higher than 0.32 GPa observed at 130–140 K,[7] lower than the 0.51–0.53 GPa observed at 110 K,[14] and slightly lower than the 0.42–0.49 GPa range observed at 125 K using a pressurization rate of 1.2 GPa/h.[53] Gromnitskaya *et al.*[14] also noted that the onset pressure for the LDA → HDA transformation was 0.4 GPa and that the transformation continued up to at least 1.4 GPa, as indicated by a significant time dependence in their data in this pressure range. It is possible that if metastable HDA at 77 K and ambient pressure is both slowly heated and pressurized, and HDA in this process, as usually observed, transformed to LDA on heating,[54] the HDA → LDA → HDA transformation sequence may be observable. The temperature in such a case would have to be increased by much more than a few kelvin as occurred here.

In an *in situ* Raman spectra study of HDA-LDA transformation at 140 K (Fig. 5, Ref. 35), the 3500 cm^{-1} broad band did not appear and the changes in the spectra were significantly different from the changes observed in experiments performed at 145 K. Moreover, the original features at 140 K and 0.9 GPa were observed only after pressurizing the LDA-HDA mixture above 0.7 GPa, and LDA changed to HDA at 0.8–0.9 GPa. This seems unusual because all earlier studies have shown that the LDA to HDA transformation is almost complete on compression to ~0.5 GPa, and the spectra in Fig. 5 of Ref. 35 show that it begins at ~0.5 GPa and ends at 0.9 GPa. We note that in an earlier study,[6] it has been found that micron-size crystals of ice I_h at 77 K on compression begin to transform to HDA at 0.7 GPa, and it is conceivable that at higher temperatures and for ice I_c this transformation would be shifted to a lower pressure.

Since our findings differ significantly from those in earlier studies and bear upon the mechanism of pressure collapse of ices I_h and I_c, we also discuss several earlier studies of relevance here. In an *in situ* study[68] of the Raman spectra of ice I_h during the course of pressure amorphization of ice I_h, it was found that the 3082 cm^{-1} peak, which was the most prominent peak of ice I_h at ambient pressure and 77 K, decreased in height and shifted to lower frequencies as the pressure was increased slowly to 0.9 GPa, and then vanished at 1.2 GPa, while the 3200 cm^{-1} small peak broadened and became most prominent at 1.2 GPa. Yoshimura and Kanno[68] attributed this finding to the formation of strong hydrogen bonds in HDA. They further concluded that amorphization of ice I_h to HDA is not a transformation to a glassy state of high-density water at 1.2 GPa but is a process of collapse of the structure at high pressures. Heating of HDA at 1.2 GPa to 218 K produced ice VI (ice IV written in their paper is probably a transcription error), and heating HDA at 1.2 GPa to 153 K and also at 0.7 GPa to 153 K made the broad peak and the high frequency shoulder more prominent, with a slight shift of both features to a higher frequency, indicating densification of HDA. These observations were reflected in a dilatometric study,[51] which led to the naming of the further densified sample as VHDA.

There is, however, an interesting feature in Fig. 2 of Yoshimura and Kanno,[68] which is worth noting. During the shifting of the ice I_h 3082 cm^{-1} peak to lower frequencies on increase in p at 77 K, the shift is highest when p is increased from 170 to 260 MPa. It is also significantly more than the total shift observed on raising p from 260 to 900 MPa, thereby suggesting that something other than simple compression occurs in the sample on pressurizing from 170 to 260 MPa. If the pressurization rate was not constant and more time elapsed in raising p from 170 to 260 MPa than at other pressures, the additional change in the sample's state would be due to the longer time taken in the 170–260 MPa range. Since the pressure-time data were not given,[68] the significance of this observation can be made clearer only by further experiments using the same or another technique.

A variety of data from experiments performed by different groups, including x-ray diffraction studies, have shown that different temperatures of the ice I_h and ice I_c, different pressurizing rates, and different times taken to perform the experiments produce different amorphs of high densities. On that basis, we suggest that the term HDA should be used in a generic sense referring to all high-density amorphous solids formed by the collapse of ice I_h and ice I_c, and not to a specific solid. It is also known[51] that the HDA formed at 77 K densifies by ~5% when heated to 160 K at a pressure higher than 0.8 GPa, and we have found that the amorphization process is time dependent, an aspect overlooked in studies in which conversion of LDA to HDA, and to a further densified state of HDA, has been achieved by pressurizing to 1.5 GPa at 125 K.[5,53]

However, an analysis of their data[5,53] shows significant difficulties with the conclusions on further densification of HDA on increase in pressure, reached in Refs. 5 and 53. To elaborate, the data for two HDAs, one normally made and one densified (in Fig. 3 of Ref. 5) show that when the samples are cooled from 125 to 77 K, ρ of the densified HDA increases by ~3.3% and ρ of the undensified HDA by 2.3%, which makes the thermal expansion coefficient of the densified HDA $\sim 7 \times 10^{-4}$ K^{-1}, which is ~1.4 times as large as that of HDA and nearly three times as high as that of pure (liquid) water at 287 K.[69] Such a high thermal expansion coefficient value for a solid at high pressures as obtained from their data is surprising.[53] For comparison, ρ of ice I_h at ambient pressure increases from 0.9292 g cm^{-3} at 173 K to 0.9340 g cm^{-3} at 93 K,[69] only by ~0.55% over a larger temperature range of 80 K and at high temperatures where the thermal expansion coefficient is expected to be relatively high. Also, their data[5,53] show that densified HDA has a higher (elastic) compressibility than HDA. As these results appear also counterintuitive, and no theoretical explanation seems to be available for this unusual behavior, we suggest that the density data of HDA and their dilatometric study[5,53] require experimental scrutiny before interpreting the irreversible HDA to VHDA transformation on increase in pressure as a distinct and "apparently discontinuous" transformation. As mentioned earlier here, recent wide angle diffraction and small angle neutron scattering studies of HDA and LDA[34] have shown that there is a correlation between the preparation conditions, microscopic structural properties, extent of heterogeneities on a mesoscopic spatial scale, and transformation kinetics and, further, that there are only two modifications that can be identified as homogeneous disordered structures, namely, VHDA and LDA, a finding consistent with the conclusion reached earlier on the basis of the thermal properties of HDAs and LDA.[2,3] Unfortunately, HDA to LDA and VHDA to HDA transformations on depressurizing the samples have not been investigated.

V. CONCLUSIONS

A detailed *in situ* study of the high-density amorph produced by the collapse of ices I_h and I_c at 130 K at very slow pressurizing rates shows that its transformation to LDA and to ice I_c differs from that of the usually studied high-density amorph that had been formed by the collapse of ices I_h and I_c on rapid pressurizing. The pressure-collapse range of ice I_c is broader and the midpoint of the range higher than those observed at 145 K,[7] which may be due to a lower temperature of our study. The LDA to HDA transformation range is also broader, and the midpoint pressure at 130 K here is higher than that at 130–140 K.[7] The latter may indicate different structures and densities of the pressure-collapsed states and LDA obtained by slow pressurizing and depressurizing, as would be expected from the kinetic, rather than thermodynamic, nature of the transformations. This seems consistent with the conclusion of Koza *et al.*[34] from diffraction studies that the degree of mesoscopic spatial scale heterogeneity in the sample can be progressively decreased when higher temperatures and pressures are applied for the sample preparation. (We find that the degree of heterogeneity is difficult to define in terms of the p-T conditions for the formation of the high- and low-density amorphs, given the irreproducibility of the data and limitations of the small angle scattering.) In this view, a slow pressurization rate at 130 K is likely to have produced a denser, lower free energy collapsed state than a rapid pressurization at 77 K, thus reducing the thermodynamic tendency to its crystallization. However, if the collapsed state were to be a partially heterogeneous mixture of nanosized crystals of various high-pressure crystalline ices, the increased density and decreased free energy would correspond to the compositional change to a larger fraction of the higher-density crystalline phase. This phase, in turn, would grow when the collapsed state is kept isothermally at a low pressure. Since high-pressure crystalline ices at ambient pressure transform to LDA on heating to $T > 120$ K and then to ice I_c, it is not surprising that the collapsed state (or HDA) transforms to LDA.

Slow depressurization at 130 K partly transforms HDA directly to ice I_c, which is kinetically preferred in the presence of ice I_c or another crystalline ice. Once the metastable high-density amorph in the sample containing ice I_c begins to dilate to LDA, the transformation to LDA continues with an increase in the pressure simultaneously as the temperature increases slowly. Ultimately, LDA collapses to HDA starting at 0.35 GPa. Thus, at a pressure of 0.34 GPa, the high-density amorph, LDA, and ice I_c at 130 K may coexist for a significantly long time. This conclusion is deduced by eliminating the possibility of the transformation of HDA to other ices, and it needs to be confirmed by *in situ* diffraction measurements precise enough to resolve the features of LDAs and HDAs of different structures. It is conceivable that there is a continuity of intermediate states formed in the transformation, and the sample is not a mixture of HDAs and LDAs.[41,42,44]

In view of the finding[37] that LDA produced by rapidly depressurizing HDA irreversibly relaxes to a hydrogen-bonded structure at $T > 120$ K with a decrease in the OH-stretching frequency (the 3100 cm^{-1} band) with no detectable change in volume, the slow depressurizing rate in our study would have produced LDA similar to that obtained after annealing in earlier studies.[37,41,42]

ACKNOWLEDGMENTS

This work was supported financially by the Swedish Research Council and the Faculty of Science and Technology, Umeå University.

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