PHYSICAL REVIEW B **70**, 184108 (2004)

Mechanisms for pressure- and time-dependent amorphization of ice under pressure

G. P. Johari
Department of Material Science and Engineering, McMaster University, Hamilton, Ontario, Canada, L8S 4L7

Ove Andersson
Department of Experimental Physics, Umea University, S-901 87, Umea, Sweden

(Received 10 June 2004; published 12 November 2004)

Amorphization of hexagonal ice under pressure at low temperatures has been studied by measuring the thermal conductivity with time, by keeping the ice in the temperature range 127–130 K and pressure range 0.79–0.88 GPa. The results have been used to examine the relative merits of the Lindemann melting and the Born instability as a mechanism for amorphization of ice. Thermal conductivity decreases continuously with time according to a stretched-exponential relation. This and the findings that, (i) amorphization pressure is lower than the available values calculated for an ideal ice crystal by using the Born theory, and (ii) amorphization of cubic ice occurs at about the same pressure as that of hexagonal ice, seem inconsistent with both mechanisms. The findings can be reconciled with the Born mechanism if the effect of the existing lattice faults and/or the lattice faults produced during the plastic deformation of uniaxially compressed ice are considered to produce a distribution of collapse pressure. It is argued that the difference between the amorphization and the low-density amorph to high-density amorph transformation pressures corresponds to the energy needed to collapse, or randomly distort, the ice crystallites to a structure whose energy spontaneously decreases by diffusion of a H_2O molecule into the first coordination shell of the amorph's known structure, and persist there as an interstitial molecule. The newly observed amorphization kinetics has a bearing on the computer-simulated inference on pressure-induced collapse and/or melting of crystals.

DOI: 10.1103/PhysRevB.70.184108 PACS number(s): 62.50.+p, 64.70.Dv

I. INTRODUCTION

When hexagonal ice at a fixed temperature between 77 K and 150 K is uniaxially compressed in a confined volume, it densifies and irreversibly transforms ultimately to an amorphous solid, which is known as the high-density amorph (HDA).[1–7] Mechanism of this pressure-induced amorphization of the ice to HDA has been postulated in two ways. In one, it has been seen as thermodynamic melting followed instantly by vitrification, because the amorphization at 77 K appears to occur at a pressure of ~1.1 GPa, in rough agreement with the extrapolated equilibrium melting curve for hexagonal ice (ice Ih) to 77 K. Accordingly, the structure of the amorphized state, HDA, is thought to be similar to that of dense water that could exist at 1.1 GPa at 77 K,[8] but has not been observed. In the second postulate, it has been seen as mechanical collapse of hexagonal ice's crystal structure under pressure.[9]

A study of the volume and temperature changes on compression of a four-component, ice-Ih oil emulsion kept at different temperatures has been interpreted by assuming that the observations can be used for pure ice. This has led to the conclusion that at $T > 160$ K, ice melts along a thermodynamic equilibrium curve, but at $T < 160$ K ice mechanically collapses.[7] Spurious thermodynamic effects that occur in an emulsion have questioned the assumption that pure ice behavior is observed in an ice emulsion.[10] However, the current view apparently supported by the emulsion study[7] is that uniaxial compression has different effects on ice Ih, which are demarked by a certain temperature of 160 K. When ice Ih is pressurized at temperature above 160 K, it melts to a high density liquid or a vitreous solid, and when pressurized at a temperature below this temperature its lattice structure collapses to HDA.[11]

According to Lindemann's classical theory,[12] thermodynamic melting occurs when vibrational displacement of atoms on heating a bulk solid exceeds a certain threshold value. In contrast, mechanical collapse of an ideal crystal lattice occurs when the crystal is subjected to a *hydrostatic* pressure. In the Born criterion[13] for the so-called "mechanical melting," increase in *hydrostatic* pressure at a fixed low temperature leads to the softening of phonon modes. This ultimately brings a crystal lattice to a state of mechanical instability, and the lattice collapses. Whether this collapse leads to a denser but randomly distorted structure or an amorph that can be obtained by cooling a liquid at ~1 GPa is not known. Although thermodynamic melting is a thermal effect, and an equilibrium phenomenon, and "mechanical melting" is not, together these have led to the suggestion that, in a pressure-temperature (p-T) plane, thermodynamic melting curve for ice Ih meets the "mechanical melting" curve at a temperature of ~160 K. Thus, pure hexagonal ice (ice Ih) under pressure melts at $T > 160$ K, and mechanically collapses at $T < 160$ K.[11] A mechanical collapse curve[11] calculated by using the Born instability criterion[13] and quasi-harmonic lattice dynamics condition has been found to be in agreement with the experimentally observed p-T conditions for amorphization of an ice emulsion.[7] These curves in which the onset pressure for apparent melting and for mechanical collapse is plotted against T are seen to yield p-T conditions for amorphization of ice Ih.[7,11]

The above-mentioned p-T boundary has been regarded as a part of the ice Ih-HDA phase diagram. However there are certain intriguing features of this amorphization: (i) Instead of being abrupt, amorphization occurs over a range of pressure as much as 0.33 GPa at ~130 K at a slow pressurizing rate[3] and this range varies with temperature and rate of pressurization[1–7] and becomes much larger for ice Ih emulsion at 77 K.[7] (ii) Cubic ice, which has no equilibrium p-T melting line, has been found to transform to HDA beginning, in the dilatometry experiments,[14,15] at a nominal pressure of 0.99 GPa at 77 K[14] and ~0.6 GPa at 145 K[15] and beginning, in the thermal conductivity measurements, at ~0.7 GPa at 130 K.[3] (iii) Cubic ice is mechanically isotropic, therefore collapse of its lattice by phonon softening alone would neither occur in the same quantitative manner as that of ice Ih nor would it produce the same amorph as the one obtained from ice Ih. (iv) Microcrystalline ice Ih amorphizes at a lower pressure than larger crystal polycrystalline ice Ih, and the width of the pressure over which amorphization occurs is less.[5] (v) At p-T conditions above 160 K, where ice Ih is postulated to melt to a high-density liquid,[7,8] one would expect the structure of the amorph to differ from that of the amorph formed by mechanical collapse at $T < 160$ K. (vi) A recent study of ice Ih amorphization has found that there is not just one HDA but a multiplicity of such amorphs.[16] We find that these features need to be considered in the context of the postulated two mechanisms for the two p-T boundaries in Fig. 1, Ref. 11.

According to the Lindemann criterion,[12] thermodynamic melting occurs abruptly at a given temperature, and according to the Born criterion[13] mechanical collapse of an ideal crystal lattice occurs abruptly at a given hydrostatic pressure. Therefore, amorphization of ice Ih is expected to occur over a narrow range of temperature at a fixed P or a narrow range of pressure at a fixed T. In an earlier study[16] we have noted that the amorphization is not abrupt. Rather, it occurs over a wide pressure range, even for pressurizing rate of 0.05 GPa/h at ~130 K when it is expected to become rapid, and the amorphization continues to progress with time within the pressure range of 0.8–0.9 GPa. Also, the onset pressure for amorphization has been found to be different by different groups using the same techniques, as reviewed earlier,[5] and the high density amorph formed by pressurizing ice Ih at 130 K to 0.97 GPa is different from the HDA formed by pressurizing ice Ih at 77 K.[17] Therefore, the time-dependence of amorphization and the variation of the onset pressure with the (unspecified) nature of the ice Ih sample are to be regarded as a characteristic of amorphization of ice Ih. We report a study of amorphization of ice Ih at different p and T, and as a function of time at these p and T, and use these observations to develop a mechanism for amorphization of ice Ih. Instead of using the volume,[1,4–7] which is an extensive property, we have chosen to use the thermal conductivity κ[3,16] which is an intensive property, to follow the progress of amorphization.[18] The study shows that the amorphization pressure is less than that calculated in Ref. 11, and measured for ice Ih emulsion in Ref. 7, and that amorhization continues at a fixed p and T in the 0.79–0.88 GPa and 127–130 K range over a period of several hours to days. We discuss these findings in terms of thermodynamic melting and mechanical collapse and suggest that if the grain boundary effects in the samples of ice Ih could be included, an incipient premelting that is unrelated to the Lindemann melting would be expected, and further that the effect of the crystal defects and lattice faults on the Born instability condition may have to be considered in the amorphization process. Finally, we compare the features of the pressure-induced *amorphization* of ice Ih and cubic ice with the features of the pressure-induced *transformation* of the low-density amorph (LDA), which had been produced by decreasing the pressure of HDA to below 0.03 GPa at ~130 K,[3,15] and which is also produced by heating HDA to ~125 K at 0.1 MPa–20 MPa.[7,8,14] This leads us to suggest that the excess onset pressure for *amorphization* of ice Ih over the *transformation* of LDA represents the energy required to randomly distort (or collapse) the ice crystallites to a structure in which an H_2O molecule can be forced to migrate by further pressurizing into the first coordination shell of its hydrogen-bonded structure, and cause its density to increase.

II. EXPERIMENTAL METHODS

The equipment and the procedure for measurements of thermal conductivity by the hot-wire technique have already been described in detail.[3] Hexagonal ice was made by freezing water contained in a ~25 ml capacity, can-shaped Teflon vessel tightly fitted inside a 45 mm internal diameter piston-cylinder assembly. The change in p and T of the sample were computer-controlled continuously during the course of the experiment. The cooling rate was 3–6 K/h and the heating rate was 6–15 K/h, at temperatures near 130 K. Ice Ih was pressurized at a rate of 0.05–0.1 GPa/h, and HDA depressurized at a rate of typically 0.1 GPa/h. These cooling, heating, pressurizing and depressurizing rates are at least one tenth of the corresponding rates used by others in studies of amorphization of ice.[1,2,4–8,14,15] Because of the slow rates used here, a single experiment lasted a period of several days. During these experiments, ice Ih amorphized slowly while its T, p, and κ were being continuously measured and the sample remained under pressure over a much longer period than in the earlier studies.[1,2,4–8,14,15] The data reported are accurate to within ±0.05 GPa for p (at 1 GPa and 100 K), ±0.3 K for T and ±3% for κ. But the precision of κ values is within 0.3%.

Pressure amorphization of ice Ih is identified by the similarity of the change in its κ with the already recognized changes in the volume,[1,4–8,14,15] dielectric permittivity,[2] ultrasonic velocity and attenuation,[19] and with our earlier study of κ,[3,16,20] where it has been called ice Ih to HDA transformation. (As discussed in detail below, properties of the high density amorph depend on the T-p path of its formation. In the earlier papers,[1–8,14–16,19,20] this distinction was not maintained and all products of pressure amorphization of ice Ih and Ic and pressure-induced transformation of LDA were called HDA, and identified as single substance. We also use henceforth the notation “HDA” to maintain this distinction and to indicate that the amorph studied here is not the one formed originally.[1]) In our earlier studies[3,16,20] it was found that, after the amorph had been formed by pressurizing ice Ih at 130 K up to 1.2 GPa, decompression at 130 K decreased its κ value, and an increase in temperature of the amorph at

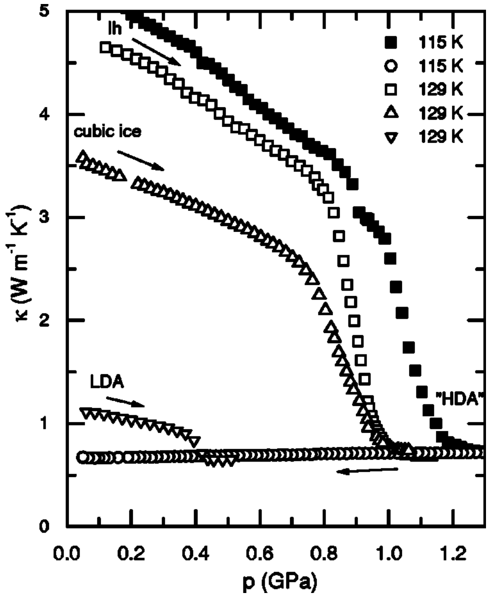

FIG. 1. Thermal conductivity of ice Ih, cubic ice is plotted against pressure showing its amorphization range and of LDA showing its transformation range to "HDA." The change on κ on depressurizing HDA at 115 K is also shown. During pressurization slow temperature variations within ±1 K cause slight variations in κ. Note the qualitative similarity of these plots with those observed for volume changes.

a fixed pressure increased it. Also, after cooling to 77 K and depressurizing to 0.05 GPa, the sample shows a slight decrease in κ of the amorph.[3,16,20] When the amorph depressurized to p close to 0.05 GPa was heated, it transformed to LDA and then to cubic ice.[3,16] Under these p-T conditions, transformation of either ice Ih or its amorphized state did not occur to another crystalline phase.[21,22]

In the detailed operation of the equipment for our study of the time dependence of the pressure amorphization, ice Ih was pressurized to a certain pressure higher than 0.78 GPa, the control program was switched from the pressure-increase mode to the fixed-pressure mode and the sample maintained at a fixed p and T by a feedback control, while its κ was being measured with time normally up to ~4 ks (70 min) and in one case much longer.[23]

III. RESULTS

Two typical plots of κ, one on both pressurizing and depressurizing of ice Ih at 115 K and the second only on pressurizing of ice Ih at 129 K, are shown in Fig. 1. Since κ for a crystalline substance normally increases with increase in pressure, the gradual decrease of κ on increasing the pressure on ice Ih and cubic ice is quite unique, and indicates, as discussed below, a molecular process that begins slowly and gradually grows in strength, leading to a more rapid decrease of κ when the lattice collapses. The onset pressure for amorphization observed here is ~0.8 GPa at 129 K, which agrees with that observed in the earlier studies.[3,16,20] A similar plot of κ against p for cubic ice at 129 K, taken from an earlier study,[3] is also shown for comparison. The onset pressure for amorphization for cubic ice is ~0.7 GPa. For comparison, we have also shown in Fig. 1 the plot of κ against p for LDA that was produced by decreasing the pressure of "HDA" to below 0.03 GPa at ~130 K.[3] Its onset pressure for gradual transformation (*not amorphization*) to HDA is 0.36 GPa, at 129 K, which is 0.32 GPa less than that of cubic ice.

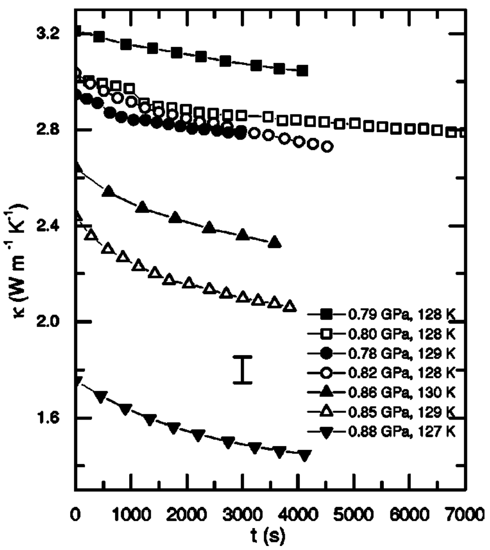

FIG. 2. Thermal conductivity of ice Ih during the course of its amorphization is plotted against time. The pressure and temperature conditions for the amorphization are labeled.

In a second set of experiments lasting for several days, measurements were made with time at several conditions of fixed p and T, seven of which are listed in Fig. 2, along with the corresponding plots of κ against time. A further set of experiments was performed in which ice Ih was kept at 128 K and 0.8 GPa and its κ was measured over a period of 106 ks (30 h). The measured value is plotted against time in Fig. 3(a). It shows a much larger decrease in κ over time and the decrease itself seems to occur in an asymptotic manner, but with little indication of an approach to a limiting value in a reasonable time.

IV. DISCUSSION

A. The time-, temperature-, and pressure-dependent amorphization

Once ice Ih has been pressurized, brought to the amorphization range and kept at a fixed p and T, the process of amorphization continues. The time dependence of thermal conductivity at these p-T conditions may indicate one or both of the two occurrences: (i) ice Ih (or cubic ice) crystallites transform at different rates by mechanism that changes their Born-instability condition, and (ii) the amorph formed is kinetically unstable, the consequent relaxation would be negligible in the early period of amorphization, because the amount of amorphous sample is negligible, and significant only when the sample is mostly amorphous. (This latter effect appears to have produced HDAs with different diffraction and other features[7] and further densification on heating

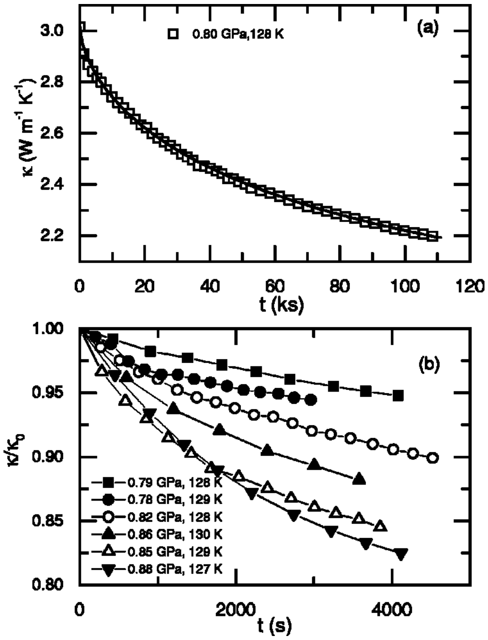

FIG. 3. (a) Thermal conductivity measured during the amorphization of ice Ih at 128 K and 0.8 GPa is plotted against time. The line represents a fit of Eq. (1). (b) Normalized values of the thermal conductivity with respect to the initial (zero-time) values for the samples kept at different pressures and temperatures is plotted against time. The pressure, temperature conditions are labeled.

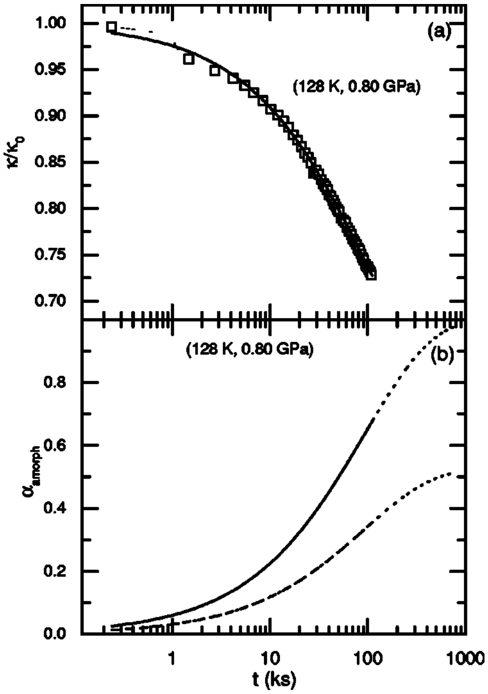

FIG. 4. (a) The normalized value of thermal conductivity measured during the amorphization of ice Ih at 0.8 GPa and 128 K is plotted against time on a logarithmic scale. κ_0 is the value at the beginning of the measurements. (b) The degree of amorphization of ice Ih at 0.8 GPa and 128 K, calculated from Eq. (2), is plotted against the time on a logarithmic scale: For the solid line κ_∞ is assumed to be 1.8 W m^{-1} K^{-1}, and for dashed line κ_∞ is assumend to be 0.7 W m^{-1} K^{-1}. The dotted lines correspond to extrapolations by using Eq. (1). (Note that the plot calculated by assuming that the sample is a mixture of ice Ih and "HDA" of $\kappa(\infty)$ of ~0.7 W m^{-1} K^{-1} does not reach a long time limiting value of 1 because the sample remains a mixture of amorph and ice at that time.)

at fixed pressure of 1 GPa.[4]) It is evident from the plots in Figs. 2 and 3 that κ decreases with time asymptotically toward a limiting value that varies with the p-T conditions. Also the rate of the asymptotic approach depends upon the p and T conditions. We express this more clearly by normalizing the $\kappa(t)$ values for each set of measurements given in Fig. 2 by the initial value $\kappa(0)$, and then plotting it against the time in the same graph. Figure 3(b) shows the plots of these normalized, $[\kappa(t)/\kappa(0)]_{p,T}$ values. It also shows that $[\kappa(t)/\kappa(0)]_{p,T}$ decreases with time and tends toward different values of $[\kappa(\infty)/\kappa(0)]_{p,T}$, for different fixed p and T. The plots in Fig. 3(b) also indicate that $[\kappa(t)/\kappa(0)]$ values at a given time differ even when the p-T conditions are almost the same, as for the plots at 130 K and 0.86 GPa and 129 K and 0.85 GPa. This means that the rate of amorphization differs even for closely similar p, T conditions. Moreover, the latter plot and that at 127 K and 0.88 GPa cross over, thus showing that there is a time reached at which $[\kappa(t)/\kappa(0)]_{p,T}$ is the same for different p-T conditions, although the rate of the decrease with time differs. Clearly a given value of κ can be reached by different p-T-t paths. Altogether these findings indicate that the initial conditions of ice Ih sample determine the rate of its amorphization and that the degree of amorphization or the κ value reached at a given p, T and t are determined by more variables than have so far been considered.

We find that the asymptotic nature of the decrease in thermal conductivity with time at 0.8 GPa and 128 K can be described by a stretched exponential relation,

$$\kappa(t) = \kappa(\infty) + [\kappa(0) - \kappa(\infty)]\exp[-(t/\tau_0)^{\beta}] \tag{1}$$

where $\kappa(0)$ is the value of κ at the instant when the fixed pressure experiment at 0.8 GPa was begun, $\kappa(\infty)$ the limiting long time value of κ, and τ_0 the characteristic amorphization time. The fit of Eq. (1) to the data is shown by the smooth line in Figs. 3(a) and 4(a). The values obtained are: $\kappa(0)=3$ W m^{-1} K^{-1}, $\kappa(\infty)=1.8$ W m^{-1} K^{-1}, $\tau_0=90.9$ ks (1500 min) and $\beta=0.6$. From these parameters we calculate that, at 0.8 GPa and 128 K, it would take 120 h to reach an amorph whose κ value is within 5% of the $\kappa(\infty)$ value of 1.8 W m^{-1} K^{-1}. Moreover, the plot in Fig. 3(a) shows that at 0.8 GPa and 128 K, κ of the amorph formed would not decrease to the same value as that of the amorph formed at 1.15 GPa and 129 K in the plot of Fig. 1, which has been previously called HDA, and will henceforth be referred to as "HDA." To elaborate, the thermal conductivity of the "HDA" formed at 1.15 GPa and 129 K, as seen in Fig. 1, is ~0.7 W m^{-1} K^{-1}, but $\kappa(\infty)$ of an amorph formed at 0.8 GPa and 128 K is 1.8 W m^{-1} K^{-1}, which is 1.1 W m^{-1} K^{-1} larger than that for "HDA." Therefore it would seem that either an amorph formed after annealing for a formally infinite time at 0.8 GPa and 128 K is different from "HDA" or Eq. (1) does not apply for the entire transformation. In view of the recent finding that κ further increases on heating the amorph formed at 1.1 GPa,[16] and that "HDA" at 1.1 GPa further densifies on heating from 77 to 165 K to an amorph whose x-ray diffraction features in the recovered state at 1 bar pressure are different from those of "HDA" recovered at 1 bar pressure,[4,24] we conclude that the final state of an amorph formed on pressurizing ice Ih depends upon the p-T conditions.

In molecular relaxation studies, Eq. (1) has been fitted to the relaxation spectra; in structural relaxation studies, it has been fitted to the enthalpy and volume changes; and in chemical reaction kinetics it has been fitted to the extent of transformation. In all these studies, the quantity β has been found to be less than 1. In dielectric and mechanical relaxations and in calorimetric structural relaxation studies, it has been interpreted in terms of a broad distribution of relaxation times[25–27] and microscopic heterogeneity in the liquids and solids,[28–30] and in chemical reaction kinetics, it has been interpreted in terms of a diffusion-controlled kinetics, dispersive kinetics, or a distribution of the reaction rate constants, an idea developed by Plonka.[31] He has concluded[31] that in the (transformation) reaction kinetics, its physical meaning is that homogenization in a viscous liquid and solid does not occur over the time scale of the transformation, and consequently a molecular level heterogeneity of the reactants and products develops within the bulk of a sample on the transformation time scale. On extending this interpretation[31] to the amorphization process of ice Ih, it means that molecular level regions of the amorph and ice Ih exist in the bulk of the sample over the transformation time scale.

B. The extent of amorphization

We now consider the decrease in κ with time in terms of the extent of amorphization. There are at least three different possibilities for the sample's state during the course of amorphization at 0.8 GPa and 129 K: (i) The sample is a mixture of Ih and an amorph whose $\kappa(\infty)$ is $\sim 1.8\ \mathrm{W\,m^{-1}\,K^{-1}}$. (ii) The sample is a mixture of Ih and "HDA," whose κ is $\sim 0.7\ \mathrm{W\,m^{-1}\,K^{-1}}$. Since $\kappa(\infty)$ of $\sim 1.8\ \mathrm{W\,m^{-1}\,K^{-1}}$ at 0.8 GPa and 129 K remains higher than the characteristic κ of $\sim 0.7\ \mathrm{W\,m^{-1}\,K^{-1}}$ for "HDA," this would mean that the sample does not fully become "HDA" even at a formally infinite time. (iii) The entire sample is an amorph that gradually transforms to its own $\kappa(\infty)$ value of $\sim 1.8\ \mathrm{W\,m^{-1}\,K^{-1}}$ at 0.8 GPa and 129 K. This last possibility is analogous to the structural relaxation of a hyperquenched glass which spontaneously densifies with time toward a state of lower fictive temperature, or to a glass of higher fictive pressure if formed by sudden pressurization.

From their studies of pressure-induced amorphization of ice Ih by using the diamond anvil high pressure cell, Hemley *et al.*[32] have reported that marked changes in the texture of the sample occur with increasing pressure. They also observed extensive fracturing of the sample occurring at ~ 0.5 GPa and the sample becomes turbid by the time pressure reached ~ 1 GPa, with new phase appearing along the fracture faults.[32] This indicates the possible existence of ice Ih together with a new phase of different texture, probably "HDA," at least up to a pressure of ~ 1 GPa. Other studies have occasionally reported that x-ray diffraction spectra of the recovered sample at ambient pressure and 77 K contain features for both "HDA" and ice Ih and they have also considered the possibility that some of the ice Ih may have formed during the handling of the samples.[33] Thus the state of the sample may be described by cases (i) and (ii) above. The state described in case (iii) seems less probable because it requires that all ice Ih amorphize abruptly or else the ice structure throughout the bulk begins to distort uniformly at a certain pressure, and thereafter the amorphous or distorted structure relaxes with time. But no study of ice Ih or cubic ice has shown that amorphization occurs abruptly,[34] and it seems inconceivable that the amorphous and crystal states would have the same thermal conductivity.[3] Therefore we would not consider case (iii) as a reliable possibility, i.e., we would not consider that the entire sample is in a kinetically unstable amorphous state which is tending, at 129 K and 0.8 GPa, *via* a series of sequentially lower κ-value (or denser) states, to its final state whose characteristic κ is $\sim 1.8\ \mathrm{W\,m^{-1}\,K^{-1}}$.

The extent of amorphization, α_{amorph}, for the above-mentioned three states can be determined by using the $\kappa(0)$, $\kappa(t)$ and $\kappa(\infty)$ values. Here, the extent of amorphization may be calculated for case (i) above, i.e., by assuming that the sample is a mixture of ice Ih and an amorph of $\kappa(\infty)$ of $\sim 1.8\ \mathrm{W\,m^{-1}\,K^{-1}}$ at 129 K and 0.8 GPa or as in case (ii) above, i.e., by assuming that the sample is a mixture of ice Ih and "HDA" of $\kappa(\infty)$ of $\sim 0.7\ \mathrm{W\,m^{-1}\,K^{-1}}$ at 129 K and 0.8 GPa (or even as in case (iii) above, i.e., that the sample is an amorph tending toward another amorphous state), all by using a single equation,

$$\alpha_{\mathrm{amorph}}(t) = \left(\frac{\kappa(0) - \kappa(t)}{\kappa(0) - \kappa(\infty)} \right)_{p,T}, \tag{2}$$

to calculate α_{amorph}. Its value calculated from both $\kappa(\infty)$ of $\sim 1.8\ \mathrm{W\,m^{-1}\,K^{-1}}$ at 129 K and 0.8 GPa $\kappa(\infty)$ of $\sim 0.7\ \mathrm{W\,m^{-1}\,K^{-1}}$ at 129 K and 0.8 GPa is plotted against the logarithmic time in Fig. 4(b). (Note that the plot calculated by assuming that the sample is a mixture of ice Ih and "HDA" of $\kappa(\infty)$ of $\sim 0.7\ \mathrm{W\,m^{-1}\,K^{-1}}$ does not reach a long time limiting value of 1 because the sample remains a mixture of amorph and ice at that time.) This plot has an extended sigmoid shape, although we can obtain only part of this shape from our data. It resembles the shapes of the plots for slow crystallization, phase transformation, chemical reactions and structural relaxation.

C. The pressure-induced amorphization mechanism

For convenience of our discussion, the p-T values corresponding to thermodynamic melting and to mechanical collapse of ice Ih taken from Fig. 1 in Ref. 11 have been replotted in Fig. 5. In it are included Mishima's data for the onset of amorphization pressure (with real pressure being 90% of the value) he had obtained for ice emulsion,[7] the data for the

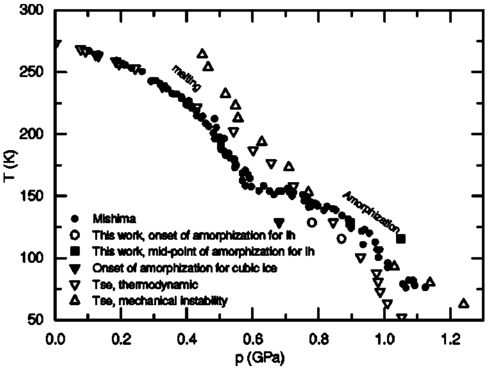

FIG. 5. Plots of temperature against pressure showing the conditions for the two apparent domains of amorphization of ice Ih. The thermodynamic melting line and the *p-T* conditions of our study and several other earlier studies are also shown. The calculated data are taken from Fig. 1 of Ref. 11 and the measured data for the onset of amorphization of ice-Ih oil emulsion from Fig. 2 of Ref. 7, where the true pressure is ~90% of the nominal pressure plotted. The data for onset of amorphization of cubic ice (129 K, 0.68 GPa) is taken from Ref. 3. The rest are the data reported here.

onset pressures for amorphization of ice Ih at 115 K (0.87 GPa) and 129 K (0.78 GPa) from Fig. 1, and the onset pressure for amorphization of cubic ice at 129 K (0.68 GPa). These pressures are accurate to ±0.05 GPa. We note that Tse,[9] and Tse *et al.*[11] have used the mid-point pressure of their calculated amorphization range and compared it with the onset pressure determined by Mishima for transformation of ice Ih emulsion to "HDA" emulsion.[7] It is to be stressed that Mishima[7] had stated that, "The pressure of the sample is ~90% of the nominal pressure."[7] Based upon this comparison, Tse *et al.*[11] concluded that "transformation to the high-density amorph is due to compaction of the ice structure *via* the filling of interstitial voids and does not correspond to the formation of a liquid-like structure."[11] Accordingly, pressure amorphization at $T < 160$ K and $p > 0.6$ GPa should occur by mechanical collapse. Considering the non-equilibrium character of the ice Ih-"HDA" demarcation line in the *p-T* plane, and the above-mentioned uncertainty of the comparison between the calculations and measurements on ice emulsions, we deduce that at temperatures in the 127–130 K range of our study, ice Ih would begin to amorphize only after the pressure, according to Fig. 5, has exceeded 0.82 (0.91×0.9) GPa. But in Figs. 1–3 here, we find that amorphization begins at ~0.78 GPa at 129 K, and it begins at ~0.68 GPa for cubic ice at 129 K. Although, the *p-T* range of our study is within the (apparent) mechanical collapse range in Fig. 5, we still need to consider the consequences of our observations for mechanisms for amorphization.

First we consider whether or not the *p-T* conditions for amorphizing a single crystal can differ from those for amorphizing a polycrystalline sample. We recall that calculations based on the Lindemann melting theory apply to an ideal single crystal without point defects or lattice faults, and this is not true for pressure amorphization of ice Ih and cubic ice samples. Johari[5] has mentioned that uniaxial compression of a ~2 mm diameter and ~3 mm long single crystal of ice Ih embedded in ~5 mm thick-wall indium cup at 77 K showed no volume decrease up to ~2 GPa, thereby suggesting that ice Ih single crystal did not collapse to "HDA." Effects that are peculiar to a polycrystalline sample also occur. For example, it is also known that grain boundaries in such samples contain a liquid-like layer, and significant premelting occurs at the three-grain and four-grain junctions when a polycrystalline material is heated in the temperature range far below its bulk melting point.[35] In this incipient melting process, the melt and solid remain at an equilibrium as the change in the solid-liquid interfacial energy compensates for the change in the bulk energy. The surface layer of ice crystals has been known to be disordered or water-like.[36] The amount of water present at the junctions of micron size grains in polycrystalline ice Ih has been determined from both experiments,[37] and calculations,[35] at ambient pressure and this amount is expected to change at high pressures, because the relative ratio of the surface energy to bulk energy changes. The piston-cylinder (uniaxial) loading on polycrystalline ice Ih in an amorphization experiment plastically deforms the ice Ih crystal grains anisotropically, converting the uniaxial load to hydrostatic pressure within less than 30 s. Like other materials undergoing this process, ice Ih crystallites reorient, the sample recrystallizes, new grain boundaries form and the population of the three- and four-grain junctions changes. This in turn would change the conditions for incipient melting at the grain junctions and grain boundaries. Although it is still the process of melting, it differs from the Lindemann melting.

According to Born's theory, a crystal becomes mechanically unstable when an increase in *hydrostatic* pressure softens the transverse acoustic phonon modes and the elastic modulus decreases. The collapse occurs homogeneously throughout the crystal lattice, and the pressure at which it occurs is determined by the manner in which the elastic constants change on compression. Born[13] had mathematically described these conditions for an ideal crystal lattice, and Tse *et al.*[11] have used his theory to calculate, in a quasi-harmonic approximation, the mechanical collapse pressure of an ideal ice Ih single crystal at different temperatures. This is necessarily a calculation for an idealized crystal. But single crystals contain point defects, impurities, and dislocations, which are expected to alter the pressure required to reach the Born instability, and polycrystalline samples contain grain boundaries and three- and four-grain junctions in which impurities segregate. Plastic deformation of ice Ih that occurs on uniaxial loading of a sample, causes its crystal grains to reorient, dislocations population to increase and dislocations to move. In this respect, it is significant to note that from their extensive studies of mechanical relaxation of single crystal ice Ih, Perez and co-workers[38] have concluded that in a single crystal of ice Ih, dislocations in the ice Ih lattice have an extended core, which is non-crystalline. Thus it seems that there are two mechanistically different occurrences in an ice sample subjected to a pressure that ultimately amorphizes it. First, the incipient melting at the intergranular regions in a polycrystalline sample and second an increase in the population of dislocation cores containing disordered arrangements of water molecules in the bulk of its single crystal.

If we were to consider, along with Tse *et al.*,[11] that after the hydrostatic pressure has been established, ice Ih mechanically collapses to "HDA" following the Born instability criterion, we would expect that the lattice faults in ice Ih crystallites would lower the collapse pressure, because these faults store energy and make the crystal's density deviate from that of an ideal crystal. Moreover, a variation in the population of the lattice faults would cause different crystallites in the polycrystalline sample to collapse at different pressures. Thus one would expect a distribution of Born instability pressures (of different crystallites) in a polycrystalline sample. This would broaden the pressure range for the mechanical collapse of the sample and, even at a very slow compression rate, full amorphization would be reached only after the pressure is high enough magnitude to collapse the near ideal ice crystal of the highest Born instability pressure. (The situation is analogous to a multicomponent crystalline composite, in which each component would collapse at its own characteristic pressure.) In this scenario, ice Ih would coexist with the amorph at formally infinite annealing time, because its $\kappa(\infty)$ of $1.8\ \mathrm{W\,m^{-1}\,K^{-1}}$ at 0.8 GPa and 128 K is higher than κ of $0.7\ \mathrm{W\,m^{-1}\,K^{-1}}$ for "HDA" formed at 1.15 GPa at 129 K, i.e., the final state would remain a mixture of (stronger) ice Ih crystallites that did not collapse at 0.8 GPa and 128 K and the "HDA" that formed by the collapse of (weaker) ice crystallites. This would also explain the observation that the onset pressure of amorphization varies with the crystal grain-size in the sample.[5]

A further effect is expected during the amorphization process, namely, that breaking of some H bonds weakens the strength of the others, because electrostatic interactions in the ices have been found to be cooperative in nature.[39,40] This would mean that at a molecular level, breaking of some hydrogen bonds as a result of structural collapse would weaken the neighboring hydrogen bonds in the ice crystal. If that were to occur, pressure amorphization of ice would become easier, i.e., its further collapse would require a smaller increase in pressure after a part of it has already structurally collapsed. Since the plots of volume and thermal conductivity against pressure have an inverted, stretched sigmoid shape, the expected effect of the weakening of the neighboring hydrogen bonds has not been observed. Therefore, the regions of collapse would seem to be small enough not to cause a sudden and rapidly increasing collapse of the whole crystal. Thus although the Born criterion remains valid for the mechanical collapse, the features of amorphization of ice Ih are altered by a distribution of the mechanical collapse pressure in a polycrystalline mass.

The observed continuous amorphization of ice Ih over such a long period of time is comparable with the apparent small step-changes in the computer simulations of Tse *et al.*,[11] but it is difficult to scale the computer simulation time of 40 ps with the macroscopic time of many hours here. We also note that experimental features of amorphization are likely to be quantitatively distinct from the computer simulation features of amorphization, and the quantities determined by the two methods may not be comparable. Nevertheless, the time dependent pressure amorphization of ice Ih at a fixed p and T may be reconciled with Born's instability criterion if occurrence of another molecular process that changes the crystallite's microstructure is included and which continuously alters, with time, the distribution of the collapse pressure at a fixed p and T. On the basis of our knowledge of plastic deformation of crystals and their recrystallization, we suggest that this process would be diffusion of defects, redistribution of impurities and dislocations and partial melting.

There is however an additional effect, namely that the randomly distorted lattice gradually changes to a p-T dependent state of HDA. Thus amorphs of $\kappa(\infty)$ higher than the κ value for "HDA" may conceivably form asymptotically with time at a rate that varies with the p-T conditions, even after all ice crystallites have collapsed. This case differs from the above described case (i), and in this case, the amorphs formed at different p-T conditions would differ in their x-ray diffraction and properties. This would be elaborated further in Sec. IV D where the collapse of LDA under pressure is discussed. Here we conclude that, (a) the rate of plastic deformation of crystallites and their recrystallization under a uniaxial stress, (b) the concentration of lattice faults in the crystallites, (c) the Born instability pressure of the crystallites and the distribution of this pressure, (d) the redistribution of impurities and dislocations and partial melting during the period of amorphization, and (e) the pressurizing rate, all determine the amorphization pressure, the pressure width of the amorphization range and the characteristic amorphization time, τ_0, at a fixed p and T.

A difference between the x-ray diffraction features has been found in a number of studies,[1,7] but reasons for the difference have been described in terms of a multiplicity of energy minima, all belonging to the energy state attributed to "HDA."[4,7] But even in the study of HDAs with differing x-ray diffraction features, there has been no report for the contamination of the sample with ice Ih. (We recognize that for an appropriate analysis, the diffraction lines from ice Ih, if present, might have been removed from some spectra.) Also recent studies have suggested that there may be a continuity of amorphs ranging from the low-density amorph (density of 0.92–0.94 g/ml at 77 K and 0.1 MPa) to the so-called very high density amorph (density 1.25 g/ml at 77 K and 0.1 MPa), and "HDA" is just one of those intermediate states. In this sense it seems that an amorph of $\kappa(\infty)$ of $\sim 1.8\ \mathrm{W\,m^{-1}\,K^{-1}}$ formed at 0.8 GPa and 129 K is also one of the states in this continuity of amorphs. The differences in the various HDAs may be partly due to the intrinsic nature of the sample in which transformation has occurred to only a limited extent and partly due to the insufficient time allowed for the sluggish transformation to reach completion.

Taken together, it seems that pressure-induced amorphization of ice Ih and cubic ice is a combined effect of incipient melting, mechanical collapse and slow change in the structure of the amorph formed. In contrast, thermodynamic melting of a polycrystalline sample begins at the grain junctions and a slight change in temperature from that equilibrium condition melts the sample completely. It is not time-dependent, but when there is a large amount of impurities dissolved in ice Ih lattice, the impurities diffuse into the submicron size premelted regions of ice by a slow process that may take months even at temperatures close to 270 K. Since premelting occurs below the thermodynamic melting curve of pure ice, which is not the case in the amorphization of ice Ih, this effect is ignored.

D. Transformation between low and high density amorphs

Finally, we discuss the consequences of our interpretation for the transformation (*not amorphization*) of LDA to "HDA." In its manifestation of decrease in volume and thermal conductivity on pressurizing, this transformation appears remarkably similar to the pressure-induced amorphization of ice Ih, cubic ice[15] or microcrystalline ice Ih.[5] It is important to note, however, that *decrease* of κ with increase in pressure for a crystalline and amorphous solid and for a liquid phase is very unusual, but the decrease in volume of these phases on increase in pressure is expected, and is invariably observed. Therefore, the particularly unusual result that κ decreases with increasing pressure abnormally for all three states, ice Ih, cubic ice and LDA,[3] and further that the behavior of thermal conductivity with changing pressure becomes normal only for the "HDA" formed from the three states, indicates that the pressure dependence of κ of ice Ih, cubic ice and LDA has a common origin. This may likely be due to the elastic softening that occurs for all these states during pressurization, as suggested by Stal'gorova *et al.*[41] But the LDA to "HDA" transformation has a lower onset pressure of 0.36 GPa at 129 K.[3] Also the apparently complete transformation of LDA to "HDA" occurs over a narrower pressure range than amorphization of ice Ih (and cubic ice), at comparable temperatures of 0.08 and 0.33 GPa, respectively, at ~130 K. It is particularly significant to note that when microcrystalline ice Ih was pressure amorphized, the onset pressure and the pressure range of amorphization was lower than for large crystal sample, and both were found to be closer to the values observed for the LDA to "HDA" transformation.[5] This indicates that for a polycrystalline sample containing micron size crystals, the amorphization onset pressure is lower and the rate of decrease in volume with increased pressure becomes faster, leading to a narrow pressure range for amorphization. It is conceivable that in a limiting case of "near zero" crystal size, the amorphization pressure of ice Ih would become comparable to the transformation pressure of LDA to "HDA."

A structural characteristic of "HDA," as determined from neutron diffraction studies,[42,43] is that there is one H_2O molecule present in its first near-neighbor coordination shell, which itself consists of four H-bonded H_2O molecules, and this H_2O molecule causes the observed ~20% higher density of "HDA." Diffraction studies have also shown that the (reverse) transformation of "HDA" to LDA that occurs at ambient pressure and 125 K is a result of spontaneous migration of this H_2O molecule out of the first coordination shell of the "HDA's structure.[44,45] It is thus intuitively expected that the pressure-induced LDA to "HDA" transformation would involve a reverse process, i.e., migration of one H_2O molecule back into the hydrogen bonded first coordination shell. More strikingly, it suggests that if LDA, for example, is pressurized to the middle of its transformation range to "HDA" and the sample is then recovered at ambient pressure and 77 K, its structure would be found to be the same as the structure of the sample of "HDA" in the middle of its spontaneous transformation range to LDA at 125 K and measured at ambient pressure at 77 K.

Both the similarity between the experimentally observed manners of transformation of LDA to "HDA" and of amorphization of ice Ih and cubic ice to "HDA," and the higher amorphization pressure for the ices relative to the transformation pressure of LDA to "HDA" indicate that the energy required for the amorphization is considerably higher than the energy required for the transformation. This suggests that amorphization of ice Ih (and cubic ice) involves two steps, first a random deformation of the ice crystal structure according to the Born criterion, which produces highly distorted H bonds, and second the migration of an H_2O molecule inside the first coordination shell which converts the randomly distorted structure to a high-density amorph. It is significant to point out that that Stal'gorova *et al.*[41] found that the LDA to HDA transformation to occur over a wider pressure range than amorphization of ice Ih (or cubic ice). Also, in their study the sample was annealed at rather (two) low pressures, 9 and 20 min, respectively, and the density increase observed for the second anneal was more than three times that observed at the lower pressure, short-time anneal. If the same mechanism was to occur in the amorphization at 1 GPa the rate of the amorphization would be much faster. This would indicate that the amorphization was not limited by the rate of the mechanism that transformed LDA to HDA.

We recognize that Born theory[13] does not suggest that collapse of a crystal would lead to an amorph. It only suggests that the instability resulting from the pressure-induced phonon-softening would cause a loss of symmetry of crystalline arrangement, and therefore merely a randomly deformed crystal lattice is produced with a structure different from that of "HDA." In this sense, it is not clear how the Born theory can be understood to cause phonon softening of an already amorphous solid, such as LDA, and collapse it to the same denser structure as formed from collapsing ice Ih or cubic ice.

We also note that in a study of pressure-induced LDA to HDA transformation, Stal'gorova *et al.*[41] have found the transformation to be time dependent when the sample was held at a fixed pressure and temperature, which indicates that the diffusion of one H_2O molecule into the first coordination shell is a thermally activated process, whose rate increases with increase in the pressure. This differs from the structural relaxation on physical ageing of amorphous solids and glasses, where all molecules undergo small-scale displacements and where the volume decrease is much smaller than observed for the ices. (For a hyperquenched glassy state, the volume decrease may be made larger, but still the rate of its decrease becomes rapid and still all molecules are displaced from their positions.) Finally, LDA to "HDA" transformation cannot be seen as Lindemann melting. We also note that the conjectured reversibility of such a transition has been put into question[16] by the recent observations of a large number of amorphous states that form between the two extremes, one extreme being LDA and the other the very high-density amorph formed by heating "HDA" at 1.1 GPa from 77 to 165 K.[4]

As already discussed, pressure-induced amorphization of ice Ih and cubic ice has been found to occur at a pressure higher than the pressure-induced transformation of LDA to "HDA." If, however, pressure-induced Born instability[13] alone was to collapse the ice crystallites which was to be followed by migration of a H_2O molecule into the first coordination shell by further rearrangement of the hydrogen-bonded structure, thus leading to the crystallite's amorphization to "HDA," then the excess of this pressure over the LDA-HDA transformation pressure would decrease with decrease in the ice Ih crystal size. It is also expected to decrease if the ice Ih and cubic ice crystals were already in a highly mechanically deformed state. Experiments may be able to determine merits of this deduction. Since "HDA" has also shown a slow transformation to LDA at ambient pressure, which occurs by slowly diffusing out of an H_2O (interstitial) molecule from the first coordination shell at a temperature-dependent rate,[44–46] it would seem that the reverse process of the diffusion of an H_2O molecule into the first coordination shell in the LDA to "HDA" transformation would involve thermally activated diffusion at high pressures. It is to be noted that the finding that heating of "HDA" at 1.1 GPa to a temperature of 165 K further densifies "HDA" has already indicated that formation of high-density amorph is a thermally activated process and that it occurs in an already randomly distorted lattice state or topologically disordered structure of a state that is one of the many distinct states between LDA and the very high density amorph.

Finally we must consider the relevance of several important computer-simulation studies of amorphization of crystals in general and the discussion of the process in terms of the Born instability and thermodynamic melting, often driven by the thermoelastic instability,[47–49] to our studies. Some of these studies are related to amorphization caused by repeated and random mechanical deformation, as in the ball-milling procedure for amorphizing metal alloys,[50] and others are related to an analysis of the onset of Born instability in a homogeneous lattice under critical loading.[47–49] Most recently, Bustingorry and Jagla[51] have provided a two-dimensional atomistic model for one-step cascade-like amorphization of crystals on *decompression*. They have considered the possibility of nucleation of a disordered phase in defective parts of crystal, following Mizushima *et al.*,[48] who had themselves discussed the lowering of the energy barrier at the defect sites in crystal-crystal pressure-induced transformation. Thus Bustingorry and Jagla[51] have concluded that collapse by mechanical instability will gradually come closer to the (equilibrium) melting line when the sample contains more and more defects. This seems to agree with the conclusion from our this study that the amorphization pressure is lowered in the presence of crystal defects. However, according to their model, the amorphization pressure cannot be lower than the thermodynamic melting line pressure. In our interpretation, if the crystal size is decreased the amorphization pressure would decrease approaching the value for the LDA to HDA transformation pressure when the ice crystals have reached nanometer size. Inasmuch as the role of crystal defects and other faults is crucial to our interpretation, computer simulations and atomistic models[47–51] may appear to be related to our study, but the consequences of these simulations and models are not the same as observed in our experiments, namely our observations of continuous amorphization with time at a fixed pressure and temperature, and of the increase in its rate with increase in the temperature. Hence, we recognize that our study would be valuable for new and further computer simulation and modeling of the pressure-induced amorphization process.

V. CONCLUSION

The observed time, temperature and pressure dependent rates of amorphization of ice Ih and the amorphization of cubic ice seem inconsistent with the thermodynamic and "mechanical' melting criteria for pressure-amorphization used for the calculations. Thus, either a mechanism other than Lindemann melting and/or Born instability is involved, or the Born-instability mechanism may be valid but there is an additional process that causes the pressure amorphization of ice Ih to depend upon the pressure, temperature and time. These processes involve reformation of lattice and microstructural defects in the samples, which reduce the pressure for the collapse and whose rate of formation determines the rate of collapse with time.

Pressure-induced amorphization of ice Ih and cubic ice appears to involve two steps, first a random distortion of the crystal lattice probably according to the Born-stability criterion, with a distribution of pressure for the lattice collapse, and second is the forced migration of one H_2O molecule into the first coordination shell of the hydrogen bonded structure of the distorted lattice or the amorph, which requires rearrangement of H_2O molecules that is made faster by an increase in pressure, i.e., it occurs by a process with a negative volume of activation. This process is therefore likely to be fast in comparison with the random distortion of the crystal lattice that occurs at higher pressures and, thus, not time limiting for the amorphization of ice and cubic ice to HDA. The first step in the amorphization process is the development of a mechanical instability, and the second is a thermally activated diffusion. In this sense, the excess pressure of amorphization of the ices over the transformation of LDA to "HDA" represents the energy needed to randomly distort the ice crystal lattice until its structure has become such as to allow the thermally activated diffusion of a water molecule in the first coordination shell of the randomly distorted structure.

ACKNOWLEDGMENTS

This study was financially supported by the Swedish Research Council. G.P.J. is grateful to NSERC of Canada for a Discovery grant in general support of his research.

[1] O. Mishima, L. D. Calvert, and E. Whalley, Nature (London) **310**, 393 (1984).

[2] G. P. Johari and S. J. Jones, Philos. Mag. B **54**, 311 (1986).

[3] O. Andersson and H. Suga, Phys. Rev. B **65**, 140201 (2002).

[4] T. Loerting, C. Salzmann, I. Kohl, E. Mayer, and A. Hallbrucker, Phys. Chem. Chem. Phys. **3**, 5355 (2001).

[5] G. P. Johari, Phys. Chem. Chem. Phys. **2**, 1567 (2000).

[6] G. P. Johari, J. Chem. Phys. **112**, 8573 (2000); **113**, 10412 (2000).

[7] O. Mishima, Nature (London) **384**, 546 (1996).

[8] O. Mishima and H. E. Stanley, Nature (London) **392**, 164 (1998).

[9] J. S. Tse, J. Chem. Phys. **96**, 5482 (1992).

[10] G. P. Johari, Philos. Mag. B **80**, 323 (2000).

[11] J. S. Tse, D. D. Klug, C. A. Tulk, I Swainson, E. C. Svensson, C. K. Loong, V. Shpakov, V. R. Belosludov, R. V. Belosludov, and Y. Kawazoe, Nature (London) **400**, 647 (1999).

[12] F. A. Lindemann, Z. Phys. **11**, 609 (1910).

[13] M. Born and K. Huang, *Dynamic Theory of Crystal Lattices* (Clarendon, Oxford, 1954).

[14] M. A. Floriano, Y. P. Handa, D. D. Klug, and E. Whalley, J. Chem. Phys. **91**, 7187 (1989).

[15] O. Mishima, J. Chem. Phys. **100**, 5910 (1994).

[16] G. P. Johari and O. Andersson, J. Chem. Phys. **120**, 6207 (2004).

[17] O. Andersson and G. P. Johari, J. Chem. Phys. **120**, 11662 (2004).

[18] Volume measurements by displacement of a piston into the ice-containing vessel yield misleading information when performed over a long period, because: (i) contraction of the components of the high pressure assembly, when the assembly as a whole slowly cools, appears as a change in volume, and (ii) the indium metal used for isolating ice from the pressure vessel gradually creeps into the space between the piston and cylinder, and this too appears as a change in volume. Both occurrences falsify the results.

[19] E. L. Gromnitskaya, O. V. Stal'gorova, and V. V. Brazhkin, JETP Lett. **85**, 109 (1997); Phys. Rev. B **64**, 094205 (2001).

[20] O. Andersson, G. P. Johari, and H. Suga, J. Chem. Phys. **120**, 9612 (2004).

[21] Because of the thermal and pressure inertia of the large and massive high pressure assembly, its operation in vacuum, and its extremely slow depressurization and cooling, neither *in situ* diffraction measurements could be made on the samples, nor could the sample be recovered for *ex situ* measurements at ambient pressure.

[22] Transformation of ice Ih to a high pressure crystalline ice or a mixture of crystalline ices at this pressure has usually not been observed (Refs. 1–7, 14–16, and 19). But when such a crystallization has been observed it has occurred implosively with a sudden decrease in pressure and increase in κ (Refs. 17 and 20). This did not occur here.

[23] The pressure was auto-restored in our experiments. This means that a decrease in volume on amorphization of ice Ih at a pressure p decreased its value to p' and the amorphization stopped. When the pressure was restored to p, more ice Ih amorphized, and the pressure again decreased to p', and so on. This is expected to continue until all ice Ih is amorphized, as occurs on thermodynamic melting and a first-order phase transformation. But here amorphization remained incomplete, and κ decreased with t even when the sample was kept subsequently at a higher p. Also, amorphization at a fixed p and T is not to be seen in the same manner as a phase transformation at ambient pressure, because the volume, κ and p all decrease in our experiment at GPa pressure, but p does not decrease during phase transformation at ambient pressure.

[24] J. L. Finney, D. T. Bowron, A. K. Soper, T. Loerting, E. Mayer, and A. Hallbrucker, Phys. Rev. Lett. **89**, 205503 (2002).

[25] C. K. Majumdar, Solid State Commun. **9**, 1987 (1971).

[26] J. T. Bendler and M. F. Schlesinger, Macromolecules **18**, 591 (1985).

[27] G. W. Scherrer, *Relaxations in Glasses and Composites* (Wiley, New York, 1986).

[28] K. Schmidt Rohr and H. W. Spiess, Phys. Rev. Lett. **66**, 3020 (1991).

[29] B. Schiener, R. Bohmer, A. Loidl, and R. V. Chamberlin, Science **274**, 752 (1996).

[30] M. Cicerone, F. R. Blackburn, and M. F. Ediger, J. Chem. Phys. **102**, 471 (1995).

[31] A. Plonka, *Dispersive Kinetics* (Kluwer, Dordrecht, 2001).

[32] R. J. Hemley, L. C. Chen, and H. K. Mao, Nature (London) **338**, 638 (1989).

[33] C. G. Salzmann, I. Kohl, T. Loerting, E. Mayer, and A. Hallbrucker, Phys. Chem. Chem. Phys. **5**, 3507 (2003).

[34] In one dilatometric study on a 1−1.5 mm thick sample of ice Ih at 77 K amorphization of ice Ih to "HDA" has been found to occur first slowly and then abruptly, reaching completion at ~1.06 GPa (Ref. 14). But we now know that when the sample is kept at a fixed pressure far above the onset pressure for a short period, the plot of the piston displacement against pressure in the amorphization range of both ice Ih and cubic ice would be vertical, suggesting a relatively abrupt decrease. A recent study has, for example, shown such a vertical decrease in Fig. 1 in Ref. 16, where κ of the sample kept for 1 h or more makes amorphization appear as if it is occurring abruptly. It is worth noting that the rate of pressurization in the earlier study (Ref. 14) had not been controlled, and that an unknown period of time was allowed between pressure-increase steps which leads to this behavior. This is also apparent in the plot for ice Ih at 115 K in Fig. 1.

[35] G. P. Johari, W. Pascheto, and S. J. Jones, J. Chem. Phys. **100**, 4548 (1994), and references therein.

[36] P. V. Hobbs, *Ice Physics* (Clarendon, Oxford, 1974).

[37] G. Salvetti, E. Tombari, and G. P. Johari, J. Chem. Phys. **102**, 4987 (1995).

[38] J. Perez, C. Mai, and R. Vassoile, J. Glaciol. **21**, 361 (1977).

[39] C. A. Coulson and D. Eisenberg, Proc. R. Soc. London, Ser. A **291**, 454 (1966).

[40] G. P. Johari and S. J. Jones, J. Chim. Phys. Phys.-Chim. Biol. **82**, 1019 (1985).

[41] O. V. Stal'gorova, E. L. Gromnitskaya, V. V. Brazhkin, and A. G. Lyapin, JETP Lett. **69**, 694 (1999).

[42] J. L. Finney, A. Hallbrucker, I. Kohl, A. K. Soper, and D. T. Bowron, Phys. Rev. Lett. **88**, 225503 (2002).

[43] S. Klotz, G. Hamel, J. S. Loveday, R. J. Nelmes, M. Guthrie, and A. K. Soper, Phys. Rev. Lett. **89**, 285502 (2002).

[44] C. A. Tulk, C. J. Benmore, J. Urquidi, D. D. Klug, J. Neuefeind, B. Tomberli, and P. A. Egelstaff, Science **297**, 1320 (2002).

[45] M. M. Koza, H. Schober, H. E. Fischer, T. Hansen, and F. Fujara, J. Phys.: Condens. Matter **15**, 321 (2003).

[46] M. Guthrie, J. Urquidi, C. A. Tulk, C. J. Benmore, D. D. Klug, and J. Neuefeind, Phys. Rev. B **68**, 184110 (2003).

[47] J. Wang, S. Yip, S. R. Phillpot, and D. Wolf, Phys. Rev. Lett. **71**, 4182 (1993); Phys. Rev. B **52**, 12627 (1995).

[48] K. Mizushima, S. Yip, and E. Kaxiras, Phys. Rev. B **50**, 14952 (1994), and references therein.

[49] D. Wolf, P. R. Okamoto, S. Yip, J. F. Lutsko, and M. Kluge, J. Mater. Res. **5**, 286 (1990).

[50] W. L. Johnson, Prog. Mater. Sci. **30**, 81 (1986), and references therein.

[51] S. Bustingorry and E. A. Jagla, Phys. Rev. B **69**, 064110 (2004), and references therein.