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Collapse of an ice clathrate under pressure observed via thermal conductivity measurements

Ove Andersson
Department of Physics, Umeå University, 901 87 Umeå, Sweden

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

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Irreversible transformation of the tetrahydrofuran ice clathrate at ~ 130 K was studied by measuring thermal conductivity κ with increase in pressure p. Initially, κ increases slowly with p up to ~ 0.75 GPa where it levels off, is roughly constant up to ~ 0.95 GPa, then decreases up to ~ 1.05 GPa. Pressure collapses the clathrate structure, plausibly beginning with lattice distortion, and κ increases at ~ 1.05 GPa in a sharp sigmoid-shape manner due to large densification until the transformation is complete at ~ 1.25 GPa. This is the opposite of that found for ice whose κ decreases first slowly with increase in p and then rapidly in an inverted sigmoid-shape manner [O. Andersson and H. Suga, Phys. Rev. B **65**, 140201 (2002)]. At 1.08 GPa and 131 K, κ increases with time t (s) according to $\sim \exp(t/2945)$, which is also the opposite of the collapse of ice [G. P. Johari and O. Andersson, Phys. Rev. B **70**, 184108 (2004)]. The difference in its behavior is attributed to strong phonon scattering from the tetrahydrofuran guest molecules. κ of the collapsed clathrate is $\sim 30\%$ less than that for the collapsed ice, which is comparable with the 25% lesser κ of the tetrahydrofuran-water solution from κ of water at ambient pressure. On depressurizing at 130 K, κ decreases progressively more rapidly and κ of the collapsed state at ~ 0.3 GPa is slightly lower than that of the as-made clathrate, showing that its original structure is not recovered.

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I. INTRODUCTION

Clathrate hydrates, or ice clathrates, are an example of inclusion compounds in which interaction between guest and host molecules stabilizes a hydrogen-bonded cagelike structure in crystals of cubic and hexagonal symmetries. Molecules of suitable size, known as "guest molecules," are confined to these cages and the structure is stable only in their presence. Since their discovery in 1810, a variety of their physical properties has been measured and theoretically analyzed and several reviews have appeared on the subject.[1–6] The density of the empty-cage structure is less than that of hexagonal ice, ice Ih. For a clathrate of the same structure, this density varies with the molecular weight of the guest molecule confined to its cages. Among these, ice clathrate of type II structure[1] containing tetrahydrofuran (THF) molecules is the most easily prepared and probably the most studied at ambient pressure. These studies have been briefly reviewed recently.[7]

Ross and Andersson[8,9] were the first to investigate the effect of pressure on THF clathrate at 130 K up to 1.5 GPa. They used thermal conductivity κ measurements and found that as the pressure p was increased, κ began to decrease slowly at about 0.8 GPa and thereafter increased abruptly at p of ~ 1.1 GPa, thus showing a dip before its rise. They also discussed the possible changes in κ of ice Ih under similar conditions. A similar study performed later on ice Ih at 77 K showed that it transforms to a $\sim 25\%$ denser (0.94 g cm^{-3} initially and 1.17 g cm^{-3} finally at 1 bar and 77 K) amorphous solid when the applied uniaxial pressure exceeds 1.2 GPa.[10] This was attributed to pressure-induced melting at the extrapolated phase boundary at 77 K. Since THF clathrate melts at 277 K and its melting point decreases much more rapidly with increase in p than that of ice Ih,[11] the clathrate was accordingly expected to melt and become amorphous solid at a much lower p than ice Ih. In an attempt to determine if THF clathrate at 77 K is also pressure melted, changes in both its volume and dielectric permittivity were studied during pressurizing to ~ 1.4 GPa and were compared against the corresponding changes observed for ice Ih.[12] Both the THF clathrate and ice Ih transformed to a state of higher density, but the permittivity of the clathrate at 77 K decreased and that of ice Ih increased, indicating that the infrared polarizability of the latter had increased. When p was then decreased to ambient, the density, which for the THF clathrate increased smoothly on pressurization, reverted close to the original value. In contrast, for ice Ih it neither increased smoothly on pressurization nor reverted to the original value on depressurization. Also, the permittivity of the clathrate increased on depressurizing much more than that of ice Ih. Thus pressurization of the clathrate to ~ 1.4 GPa produced a state that could not be recovered at 1 bar and 77 K.

A subsequent dilatometry study of the THF clathrate at 77 K showed[13] that on pressurization, its volume abruptly decreased (or piston displacement increased) by $\sim 19\%$ at 1.3 ± 0.1 GPa. Also, when p was reduced from 1.72 GPa to 70 MPa in 10 min and the sample recovered at 77 K at ambient pressure, the results were the same as for the starting material, "indicating that the high-pressure phase had transformed back to the structure II hydrate during recovery of the sample."[13] Moreover, on *in situ* heating from 77 to 129 K at 210 MPa the sample recovered $\sim 85\%$ of its initial volume. Thus the phase formed on transformation at 1.3 GPa could not be recovered at 77 K and ambient pressure. It also did not fully revert to the original clathrate at $T < 129$ K and $p > 0.2$ GPa. In a recent *in situ* study, Suzuki[14] found that as p is increased, THF clathrate at 77 K undergoes a rapid first-order-like transformation beginning at p of ~1.3 GPa with an ultimate volume decrease of ~20%. In his study, the sample that was annealed at 1.5 GPa at 150 K and then recovered at 1 bar and 77 K showed no sharp x-ray diffraction features of a crystal lattice. Also, *in situ* studies of the Raman spectra at 70 K at different p showed that broad peaks attributable to the (denser) amorphized THF clathrate begin to appear at 1.3 GPa. But the peak attributable to the crystalline clathrate disappeared only when p was increased to 1.8 GPa. This indicated that the sample amorphized in the 1.3 to 1.8 GPa range, and the amorphized and crystalline clathrates coexist in this pressure range. Suzuki[14] conjectured that the THF clathrate collapsed to a structure similar to the one that forms on collapse of ice Ih even though the O-H stretching Raman feature for the *in situ* annealed high-density amorph (HDA) of water at 1 bar in Fig. 2(d) slightly differs from the corresponding spectra of THF clathrate at 1.8 GPa at 70 K in Fig. 3 of Ref. 14. Thus it seems that annealing produced a denser and more stable collapsed state of the clathrate in a manner qualitatively similar to the annealing of HDA in the range 130–160 K at 1 GPa, where the dielectric relaxation time is less than one minute.[15] (Note that a phenomenologically distinct spontaneous process during heating an HDA sample at 1.17 GPa to 130 K at 3 K/min appeared to have fully relaxed it.[16]) HDA produced by isothermal pressurization of ice at 77 K relaxes on heating at 1 GPa irreversibly to a denser, thermally more stable state that transforms to low-density amorph (LDA) at a higher temperature on heating at low pressures.[17]

Ross and Andersson[8] had established that the THF clathrate transforms on compression to 1.5 GPa at 130 K. However, despite numerous studies on pressure collapse of ice Ih, Ic, and other solids that followed their report, it is not certain how the clathrate transforms and why, unlike HDA formed at 77 K, the pressure-collapsed clathrate produced under similar conditions is *not* recoverable at 1 bar and 77 K. Studies of a variety of organic solids have also shown that their collapsed state is not recoverable at ambient pressure. Here we report a detailed study of the collapse of THF clathrate by *in situ* measuring κ. We also report a study of its isothermal transformation under pressure and the effect of pressure cycling on the transformed states.

II. EXPERIMENTAL METHODS

Tetrahydrofuran (puriss. p.a., 99.9%, less than 0.005% water) was purchased from Sigma-Aldrich Chemicals. Two solutions in pure water (Milli-Q® Ultrapure WaterSystems) were prepared by weighing separately to obtain $THF\cdot 16.8\ H_2O$ and $THF\cdot 16.65\ H_2O$, respectively, and then transferred to the sample cell. The cell was cooled to about 265 K at ambient pressure and then heated to a few degrees below the THF clathrate's freezing point of 277.4 K, where it was kept for more than 1 h to allow the solution to freeze completely to clathrate.

The method and the equipment used to measure κ are the same as used for the study of crystalline and amorphous solid water.[18–20] Briefly it uses a circular-shape hot wire. The sample cell used 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 a piston-cylinder type 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 via a built-in refrigerator, which uses a closed helium gas cycle.[21] The vacuum needed for its operation eliminates frost formation and hence the resulting friction between the piston and vessel is greatly reduced. Pressure was determined from the load/area with correction for friction. This correction was determined by an *in situ* experiment using the pressure dependence of the resistance of a manganin wire. The temperature was measured by a chromel-alumel thermocouple, which was calibrated against a commercially available silicon diode thermometer.

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 the shape of a circular ring of constant radius within the Teflon cell. The hot wire surrounded by the solid was heated by a 1.4 s long pulse of nominally constant power, and its electrical 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. The analytical solution for the temperature rise with time was fitted to the data points for the hot-wire temperature rise and κ was determined. Its inaccuracy was ±2% at 298 K. However, as the temperature coefficient of electrical resistance of the (nickel) hot wire decreases with decrease in the temperature, the inaccuracy of the measured κ 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. It is noteworthy that in comparison with measurements on ice Ih, failure of the several-days long experiments due to unpredictable breaking of the hot wire was less frequent in this study than in the study of ice Ih, and only one in two measurement setups was aborted.

III. RESULTS

The THF solution of appropriate concentration was initially cooled and heated at ambient pressure to ensure that it froze completely to form the clathrate. Differential thermal data of $THF\cdot 16.8\ H_2O$ showed a very small crystallization exotherm at 269 K on cooling, thus indicating that a small amount of water froze to ice Ih and not the clathrate. Therefore another composition, $THF\cdot 16.65\ H_2O$, was investigated. It completely froze to the clathrate. Thereafter, p was raised to a value within the range 0.02–0.05 GPa and the sample cooled to about 110 K. The results showed that p of at least 0.05 GPa was needed to ensure good thermal contact between the wire probe and the sample down to 110 K. For comparison with the study of pressure collapse of ice Ih, the temperature was subsequently increased and isothermal experiments were performed at 130 K and p of up to ~1.3 GPa. The first set of κ values obtained on pressurizing the THF·16.8 H_2O clathrate at a rate of 0.17 GPa/h is shown in Fig. 1(a). The measured κ values for this composition were about 1.5% higher than the values obtained for THF·16.65 H_2O. It can be due to the small ice content, but the difference is also within the experimental error and the results agree to within ±1% of the κ values reported by Ross and Andersson[8,9] for THF·16.59 H_2O at 130 K and 0.1 GPa. In Fig. 1, the change in the clathrate's κ with increasing p has been divided into three regions. In region 1 there is a gradual increase with increasing p up to ~0.75 GPa. In region 2 there is first a roughly constant κ and then a decrease at ~0.95 GPa, leading to a local minimum at ~1.1 GPa and κ=0.45 W m^{-1} K^{-1}. Lastly, in region 3 there is a sigmoid-shape rise to κ=0.51 W m^{-1} K^{-1} at ~1.3 GPa.

After reaching 1.3 GPa, the sample was depressurized at a rate of 0.2 GPa h^{-1} to 1 GPa during which its κ, also plotted in Fig. 1, slightly decreased. As a precaution against accidental loss of the temperature control overnight, it was then kept at 1 GPa and cooled overnight to 110 K in 10 h and then heated back to ~130 K in 1 h. The procedure produced a discontinuity in the κ-p plot in Fig. 1. When the sample was then continuously depressurized from 1 GPa at 0.17 GPa h^{-1} rate, it showed two regions, 4 and 5, in which its κ decreases with decreasing p. In region 4, $d\kappa/dp$ becomes progressively more positive and the original κ value is reached at p of ~0.35 GPa. In region 5, κ decreases below the original clathrate's value in region 1. As the second pressure cycle was begun, the hot wire broke, and the experiment terminated. For comparison, Fig. 1(b) shows the plot of piston displacement against p for the clathrate at 77 K as reported by Handa *et al.*[13] and by Johari and Jones[12] for different volumes of the clathrate. Figure 1(c) shows the plot of the dielectric permittivity at 1 kHz and 77 K.[12] To compare against the corresponding behavior of ice Ih, a plot of the κ of ice Ih against p taken from our earlier study[22] is shown in Fig. 2, along with the clathrate data from Fig. 1. It shows their relative change in κ, as well as the ultimate value of κ reached at 130 K and ~1.3 GPa.

In a subsequent experiment, the THF·16.65 H_2O clathrate was compression cycled and its κ against p plot is shown in Fig. 3(a). The local minimum in κ appears here at a slightly lower p of 1.05 GPa. The sample at 130 K was kept at a fixed p of 0.9 GPa for 1.3 h and its κ was measured with time t. Its value remained constant. The sample was thereafter annealed at a fixed p of 1.1 GPa, which is near the local minimum in κ, for 2.2 h. Its κ increased from 0.46 W m^{-1} K^{-1} to 0.50 W m^{-1} K^{-1}, which is to be compared against the increase in region 3 from Fig. 1. After annealing, increasing p to ~1.3 GPa at the rate of 0.17 GPa h^{-1} increased its κ to 0.51 W m^{-1} K^{-1}.

The sample was depressurized from 1.3 to 0.3 GPa at 0.17 GPa h^{-1} rate. Its κ decreased progressively more rapidly as in region 4 of Fig. 1. Within the experimental error of ±2%, the values in region 4 in Figs. 1 and 3 are the same. In region 5, which starts at about 0.35 GPa, κ decreases by 5% over a small p range of 0.05 GPa. This indicates a transition, after which κ tends to slowly increase on decompression toward the value for the as-made clathrate. The sample was kept at fixed p of 0.2 GPa for 1 h, during which κ did not change.

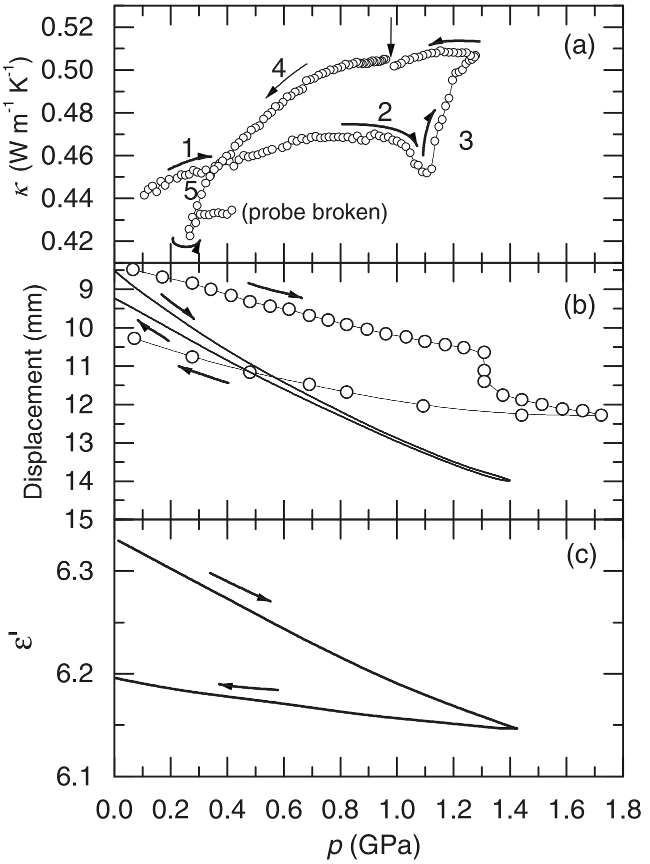

FIG. 1. (a) Thermal conductivity of the THF·16.8 H_2O clathrate at 130 K is plotted against pressure. Arrows indicate the direction of pressure change and the regions are marked. The vertical arrow near 1 GPa indicates the pressure at which the sample was kept at a fixed pressure, cooled to 110 K during the night, and heated back to 130 K in 1 h. (b) The plot of piston displacement against pressure for the THF clathrate at 77 K as reported by Handa *et al.* (Ref. 13) and Johari and Jones (Ref. 12), where the latter has been shifted vertically to the same starting displacement as that for Handa *et al.* (Ref. 13). (Note the volumes of the clathrate in the two studies differ. Therefore, the change persisting at ambient pressure in the two studies is qualitative and not comparable.) (c) The plot of the dielectric permittivity at 1 kHz and 77 K, which was measured in a concentric electrode dielectric cell simultaneously as the piston displacement data (Ref. 12). In general, the profiles indicating pressure collapse of the clathrate in the three studies differ. Since the rate of p increase and decrease and the annealing of the sample at 77 K had not been controlled in earlier studies (Refs. 12 and 13) and no further details are available, we speculate that the difference between these profiles arises from (i) the slow occurrence of the clathrate's collapse as evident from the data in Fig. 5, as discussed here, (ii) the broader pressure range of the collapse in comparison with that of ice Ih, and (iii) the temperature and pressure histories of the samples. Also, the manner of uniaxial to hydrostatic pressure transfer in the narrow tube-shape sample in a concentric electrodes dielectric cell at 77 K in Ref. 12 differs from that in a disk-shape sample in Ref. 13 and here.

On repressurizing from 0.2 to 1.0 GPa in region 6 of Fig. 3(a), κ did not increase significantly. At p above 1 GPa, it

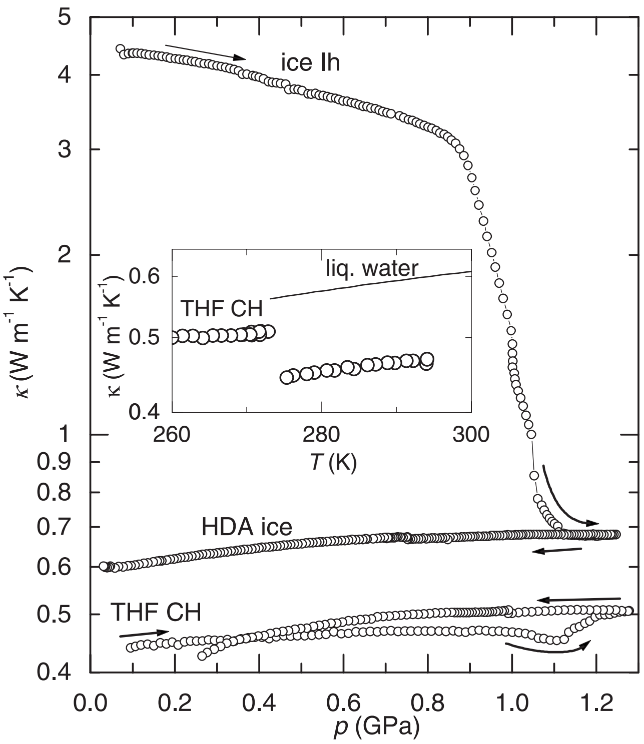

FIG. 2. The plot of thermal conductivity (at $\log_{10}$ scale) of ice Ih at 130 K against pressure during both the pressurizing and depressurizing cycles (Ref. 22), as marked by the arrows. For comparison, the data for the clathrate from Fig. 1 are plotted on the same scale. The inset shows results for the THF clathrate hydrate at 0.05 GPa and its melt and pure water (Ref. 28) at atmospheric pressure.

showed a sigmoid-shape increase reaching 0.5 W m^{-1} K^{-1} at 1.2 GPa in region 7. Thus in the pressure cycle in Fig. 3(a), κ reaches a local minimum on first pressurizing, a transition begins at p of $\sim$0.35 GPa on depressurizing, and the local minimum is not observed on repressurizing.

Figure 3(b) shows the corresponding plots for a new THF$\cdot$16.65 H_2O clathrate sample at T of 130 K, where the paths 1 to 7 are the same as well as the results to within the inaccuracy. An additional annealing was done at 0.48 GPa for 1.3 h in region 6, during which κ remained constant.

The extent of reversibility of the change in κ observed in region 4 of Fig. 3(a) was studied in detail by cycling p in the sequence 1 GPa$\rightarrow$0.4 GPa$\rightarrow$1.2 GPa$\rightarrow$1 GPa, the lower p limit of 0.4 GPa of the cycle prevented the transformation that begins at $\sim$0.35 GPa during the depressurization in region 5 in Fig. 3(a). The results are shown in Fig. 4(a). The change in κ occurs with a large hysteresis, but after completion of the cycle, κ returns to the initial value. After the sample had been pressure cycled twice up to $\sim$1.3 GPa at 130 K, it was kept at a fixed p of 0.05 GPa and heated. The measured κ is plotted against T in Fig. 4(b). It increases more rapidly in the T range of 138–144 K and becomes identical to that measured for the original clathrate made by cooling the solution.

In the pressure cycle shown in Fig. 3(a), the sample was annealed by keeping at 1.08 GPa and 131 K, a condition at which the κ-p plot shows a local minimum, and its κ measured with time t. The plot of κ against t in Fig. 5 shows that it increases asymptotically, according to the relation

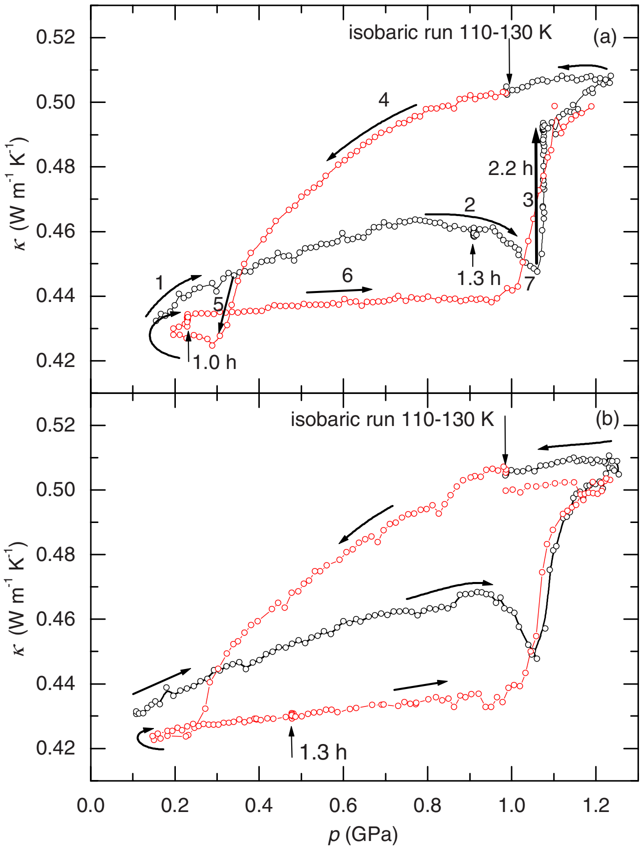

FIG. 3. (Color online) (a) Thermal conductivity of THF$\cdot$16.65 H_2O clathrate at 130 K is plotted against pressure during pressurizing and depressurizing, as marked by the arrows. Vertical arrows pointing up show the pressures of annealing. The long arrow shows the change when the sample was kept at 131 K and 1.08 GPa for 2.2 h. (b) The corresponding plot of a new sample in which the once pressure-cycled THF$\cdot$16.65 H_2O clathrate sample was kept at 0.48 GPa for 1.3 h (in region 6), and its κ did not change with time.

$$\kappa(t) = \kappa(\infty) + [\kappa(0) - \kappa(\infty)]\exp[-(t/\tau_0)], \qquad (1)$$

where $\kappa(0)$ is the initial value of κ at 1.08 GPa and 131 K, $\kappa(\infty)$ the limiting long-time value, and τ_0 is the characteristic transformation time. The best fit of Eq. (1) to the data was obtained for $\kappa(0)=0.459$ W m^{-1} K^{-1}, $\kappa(\infty)=0.497$ W m^{-1} K^{-1}, and $\tau_0=2.9$ ks. This fit is shown by the smooth line in Fig. 5.

IV. DISCUSSION

A. Reversible change in thermal conductivity with *T* and *p*

In general, thermal conductivity of crystals strongly decreases with increasing T, typically according to $\kappa \sim T^{-1}$. Ross and co-workers[23,24] found that κ of ice clathrates instead *increases* reversibly with T, which is similar to that observed for a glassy or an amorphous solid. The increase is not likely to be associated with the orientational disorder of water molecules in clathrates because the ices, in which there is also an orientational disorder of water molecules, show a

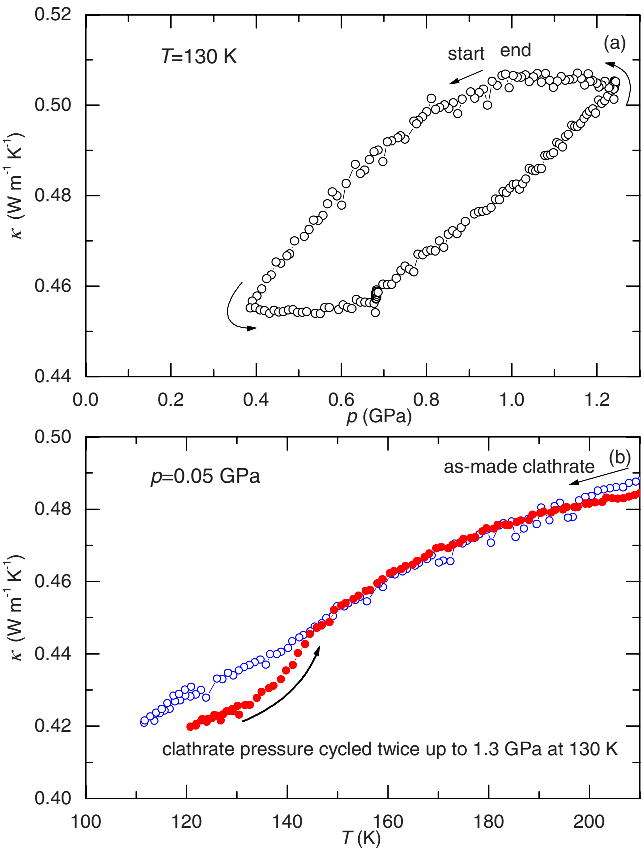

FIG. 4. (Color online) (a) Thermal conductivity of THF·16.65 H_2O at 130 K is plotted against pressure during a pressure decrease and increase in region 4 of Fig. 3(a), as marked by the arrows. (b) Thermal conductivity of the as-made clathrate (on cooling) and the state formed after pressure cycling twice in the range 0.05–1.3 GPa at 130 K (on heating).

normal crystal-like behavior[19] and it has been found that the orientational or proton ordering does not change the glasslike behavior of the clathrates.[25] Both findings suggest that orientational disorder does not act as a predominant source for phonon scattering.[25] The origin for the glasslike variation of κ with T is not fully understood, but guest-host coupling[26] in clathrates is considered to be important and it probably causes resonance scattering.[27] It should also be noted that κ of the THF clathrate is only ~15% more than that of the corresponding melt, as is shown in the inset to Fig. 2. For comparison, κ of the clathrate melt, which is a THF aqueous solution, is ~25% lower than that of pure water at 295 K and ambient pressure[28] (Fig. 2). This difference is about the same as that between the collapsed clathrate and the collapsed ice Ih (HDA) at 130 K and 1.2 GPa, which differ by ~30% in Fig. 2.

For a more detailed discussion of κ, we use the familiar Debye formula[29]

$$\kappa = \frac{1}{3}\rho c_V v \ell, \tag{2}$$

where ρ is the mass density, c_V is the specific-heat capacity per unit volume, v is the velocity of the heat carriers, and ℓ

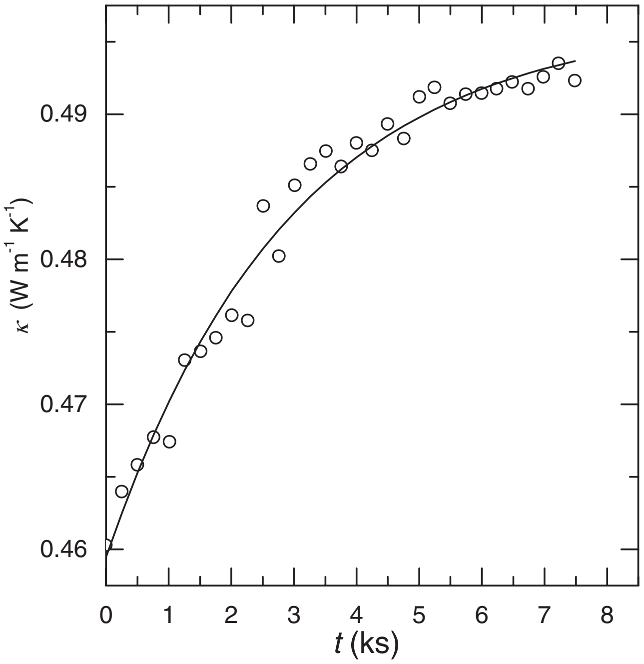

FIG. 5. Thermal conductivity of the THF·16.65 H_2O clathrate at a fixed pressure of 1.08 GPa and 131 K is plotted against time. The p, T condition refers to the long vertical arrow seen in Fig. 3(a). The solid line represents a fit of Eq. (1).

is the mean-free path. In principle, both changes in κ with p and/or with T, and as a result of pressure collapse of the crystal, can be analyzed in terms of Eq. (2). Here, we first discuss the change of κ that occurs reversibly with change in p and T.

It is known that the mean-free path for phonon propagation in single crystals and the usual polycrystals is limited mainly by three phonon-phonon Umklapp scattering.[30] Since the number of phonons that can participate in Umklapp scattering processes increases proportionally to T at high temperatures, the mean-free path is inversely proportional to T. Neglecting the variation in ρ, c_V, and v with T, this corresponds to the normal $\kappa \propto T^{-1}$ behavior. In extremely fine crystals, approaching the micron size, and in crystals containing a large population of defects, other scattering mechanisms contribute, but still their $d\kappa/dT$ remains negative at T close to or above the Debye temperature. The glasslike thermal conductivity of ice clathrates, i.e., their positive $d\kappa/dT$ appears therefore as an extreme deviation from the normal $\kappa \propto T^{-1}$ behavior for a crystal. In the absence of any other mechanism, it has been attributed to strong scattering by the guest molecules.[26,27] The additional scattering decreases ℓ significantly until it becomes of the same order as the lattice spacing and it would not decrease further even when scattering from other sources increases with increase in T. Since ρ and v only weakly depend on T, κ will vary as c_V varies with T, i.e., it would increase weakly with T. Krivchikov *et al.*[31] recently showed that at $T > 100$ K, the mean-free path of the phonons in the THF clathrate is considerably smaller than the lattice parameter and no longer changes on further heating. There is also another aspect to this finding that may be related to the unit-cell size of a crystal. The unit cell of THF ice clathrate is in space group $Fd3m$ with 1.73 nm dimension. It contains 136 water molecules forming 16 small and 8 large cages[1,2] with the THF molecules in the large cages, one per cage. Thus its space group of 1.73 nm contains 144 molecules in all. If κ was to vary with the size of the unit cell in relation to the mean-free path, it would seem to reach the glasslike T dependence for those crystals which have a large unit cell. Dharma-wardana[32] considered this aspect but Ross[33] argued that the model does not predict the positive $d\kappa/dT$ without further discussion.

Similar arguments based on Eq. (2) are applicable for the increase in κ with p at a fixed T, as seen in Figs. 1(a) and 3. Here, the change of κ with p is determined by the changes in c_V, ρ, and v. The mean-free path remains roughly constant or may even increase slightly as the crystal becomes more harmonic. Although c_V decreases slightly with increase in p, the increase in ρ and v more than compensate for this decrease and $(d\kappa/dp)_T$ becomes positive.

B. Change in thermal conductivity during the pressure collapse

Crystal-crystal phase transformation of THF clathrate at 240 K has been known to occur at high pressures,[8] and more recently a transition has been detected to a new space filling polyhedron in THF clathrate at 293 K and 0.8 GPa.[34] The thermal conductivity increases by ~30% sharply at ~0.3 GPa when crystal-crystal transformation occurs at 240 K (Fig. 5 in Ref. 8). It is not certain whether this is reversible on decompression. In Fig. 3, an overall increase in κ occurs in the 0.9–1.25 GPa range at 130 K, and it is only by ~10%, from 0.46 to 0.52 $\mathrm{W\,m^{-1}\,K^{-1}}$. Moreover, a minimum in κ appears at 1.05 GPa immediately before the rapid increase. Therefore the change in κ observed here at 130 K is not related to those observed earlier at 240 and 293 K.[8,34] In the light of Suzuki's recent Raman spectra studies,[14] it is due to collapse of the clathrate structure that leads to an apparent amorphization.

The change in κ on pressure-induced collapse of THF clathrate may also be discussed in terms of the changing parameters of Eq. (2). For this purpose, we first consider the appearance of the minima at 1.05 GPa in Fig. 3. As the sample densifies in this process, c_V would decrease as ρ increases causing the Debye temperature to increase, v would increase and ℓ would decrease if the sample amorphizes. The resulting decrease in κ is expected to be much smaller than that for the pressure collapse of ice Ih, in which the phonon mean-free path is limited by phonon-phonon scattering, and also because κ of the THF clathrate is already low, about 1/10 of that of ice Ih. For a brief comparison, κ decreases to 1/5 of the value at the beginning of the collapse of ice Ih, which is attributable to a very large decrease in ℓ when the main scattering source changes from phonon-phonon scattering to scattering from structural disorder. In the clathrate hydrate, the main scattering source appears to be so dominant that on its structural collapse, ℓ will not decrease much and the increase in ρ and v can determine the ultimate change in κ. Thus, the beginning of the slow decrease in κ at p near 0.75 GPa in region 2 in Figs. 3(a) and 3(b) followed by a rapid decrease to a local minimum is likely due to a slight decrease in ℓ as the crystal lattice deforms and the empty cages in its structure begin to collapse. But as ℓ cannot continue to decrease without limit, it reaches its minimum value, and thereafter κ begins to increase as ρ and v increase with increase in p. This interpretation seems to be consistent from the findings in the dielectric properties measured during the collapse of this clathrate. These had shown that strong densification occurs in the 1.0–1.2 GPa range,[35] in qualitative agreement with the increase of κ observed in the 1.05–1.15 GPa range in Fig. 3. We conclude that the change in κ with p during the pressure collapse of THF clathrate does not mimic the pressure collapse of ice Ih, as evident from the plots in Fig. 2, because of its already low value of ℓ that can decrease only up to a certain limit, and then κ increases as the collapsed state densifies on further compression. The negative effect of decreasing ℓ and c_V on κ with increasing p becomes equal to positive effect of increasing ρ and v with increasing p at about 1.05 GPa where the minimum in Fig. 3 appears. The already low value of κ attributed to small ℓ has been explained above in terms of strong phonon scattering caused by the THF guest molecules in the as-made clathrate and confirmed by Krivchikov *et al.*[31] from measurements of κ over the T range of 2–220 K.

C. Density dependence of the thermal conductivity

The change of κ with density of a phase is described in terms of the magnitude of the Bridgman parameter g, which is written as $g=(d\ln\kappa/d\ln\rho)_T=[(d\ln\kappa/dp)/\beta]_T$, where ρ is the density and $\beta=(d\ln\rho/dp)_T$ is the compressibility. β for the THF clathrate is not known but it has been measured accurately for ice Ih at 130 K and ambient pressure and is listed as 0.113 $\mathrm{GPa^{-1}}$.[36] We regard it as approximately independent of p for ice Ih and use Whalley's (Ref. 37) approximate calculations showing that β of a clathrate is 1.162 times that of ice Ih. Thus $\beta=0.131\ \mathrm{GPa^{-1}}$ for the clathrate. A linear fit of our ln κ against p data in the range up to 0.7 GPa yields $(d\ln\kappa/dp)_T=0.123\ \mathrm{GPa^{-1}}$. Thus, $g=0.9$, which is small in comparison with that for other crystals, and g tends to increase with increasing structural order.[24] For example g of liquids is about 3,[24] it is in the range 1.5–4 for amorphous polymers,[38] in the range 3–6 for orientationally disordered crystals, and g is in the range 6–10 for ordered crystals.[24] Hexagonal ice seems to be an exception for which g is negative,[24] −4.4 at 130 K.[39]

When a solid phase transforms, or a crystal under compression collapses, g is expected to change as the structure changes, but the relation is complicated by the change in the phonon scattering from other sources that appear or disappear, or else is effective differently in different phases. Figure 3 shows that for the collapsed clathrate, the quantity $(d\ln\kappa/dp)_T$ is slightly larger than that for the as-made clathrate. A linear fit of our ln κ against p data in the 0.4–0.9 GPa range yields $(d\ln\kappa/dp)_T=0.183\ \mathrm{GPa^{-1}}$. β for the collapsed THF clathrate is also not known. For the sake of argument, if it is taken to be 50% more than that of the as-made clathrate, g would be 0.9, and if it is taken to be 50% less, g would be 2.8. Even within these limits g of the collapsed state remains small, but still it is likely to be somewhat larger than g of the as-made clathrate. Thus, g increases during the collapse of the clathrate, which is the same behavior as has been observed during the collapse of ice Ih, where g increases from -4.4 for ice Ih to 1.7 for the high-density amorph.[39] This shows that g of the collapsed state of both ice Ih and THF-clathrate hydrate is higher than of their crystal phase. Since the collapsed states are structurally more disordered, this is the opposite of the usual finding that g increases with increasing structural order.

D. Kinetics of pressure-induced collapse by thermal conductivity

In Fig. 5, the data obtained during annealing the clathrate at fixed p near 1.1 GPa and 130 K show that κ increases as the collapse of the structure progresses. Such a time dependent collapse has been observed also for ice Ih (Refs. 40 and 41) where it has been argued that structural collapse progresses with time at different rates, depending upon T and p. But in the case of ice, κ decreases as transformation progresses. This is opposite to that found for the clathrate in Fig. 5. This may be understood by the dominance of density and sound velocity increase as the clathrate structure collapses, in contrast to the dominance of the mean free path decrease as the ice Ih structure collapses, as discussed above. Kinetics of transformation is of first order according to the fitting of Eq. (1), as for ice Ih, and although a direct comparison is difficult to make owing to the difference in the transformation p and T, the kinetics of the clathrate collapse is faster than that of ice Ih. To elaborate, for the clathrate at 131 K and 1.08 GPa, which is close to p at the local minimum in κ in Fig. 3(a), τ_0 of Eq. (1) is 0.8 h. The corresponding $\kappa(\infty)$ of 0.497 W m^{-1} K^{-1} is close to the κ for the fully densified clathrate and its magnitude is typical of an amorphous solid. In contrast, for ice Ih at 128 K and 0.8 GPa, which is p immediately after the collapse begins at $\sim$0.78 GPa, τ_0 is 25 h. The collapse continues for several days and $\kappa(\infty)$ does not seem to reach a low-enough value expected for an amorphous solid.[40,41]

E. Irreversibility of transformation on decompression

The plot in region 4 in Fig. 3(a) shows that on decompressing the collapsed state of the clathrate, κ decreases, especially rapidly at p near 0.35 GPa (region 5). This is typical of a transition that occurs slowly even with the slow depressurizing rate used here and with a large apparent hysteresis. Such a slow transformation on depressurizing of the collapsed state of THF clathrate appears to have remained unresolved. Handa *et al.*[13] concluded that the only possible means of recovering the high-pressure phase will be to perform the experiments at $T < 77$ K in order to avoid relaxation back to the crystalline form. But Suzuki[14] instead annealed the transformed phase at 1.5 GPa and 150 K and then recovered the apparently untransformed phase at 1 bar and 77 K. He found it to be amorphous.

There are considerable differences between the results obtained on compression of the as-made clathrate and of the pressure-cycled sample, as seen in regions 6 and 2 of Fig. 3. On that basis, we conclude that the collapsed state did not fully revert to the same structure as the original as-made clathrate. The lower values for κ of the pressure-cycled state indicate that some disorders persist, possibly due to THF molecules outside the large cages and/or lattice distortion of the crystal itself. In that sense, the rapid change in κ at p near 0.35 GPa would indicate partial reversion to the original state of the clathrate structure. The progressively more positive $d\kappa/dp$ with decreasing p in region 4 indicates that this reversion might be gradual and it may have begun at $p > 0.35$ GPa. To investigate this possibility, we consider the pressure cycle 1 GPa$\rightarrow$0.4 GPa$\rightarrow$1.2 GPa$\rightarrow$1 GPa shown in Fig. 4(a), in which the lowest pressure was kept above $\sim$0.35 GPa to prevent the rapid transformation. The measured κ in the pressure cycle shows a significant hysteresis. This is partly inherent to such methods because the error in p due to friction reverses sign when pressurization changes to depressurization. Since the hysteresis in κ here is unusually large, this indicates that any transformation on depressurization occurs slowly also at a higher p than that for the abrupt change ($\sim$0.35 GPa), thus leaving the state only to a small extent transformed at a higher p. Therefore, for the rates of pressurization and depressurization used here, the slightly transformed state follows a different pressure path to the (collapsed) high-density state than the path for the original clathrate shown in Fig. 3. We conclude that the wider loop of the κ-p plot in Fig. 4(a) than expected from pressure hysteresis alone indicates that reorganization of the clathrate structure by diffusion of water and THF molecules in the collapsed state does slowly occur at $p > 0.35$ GPa on depressurizing.

We recall that complete transformation of aqueous THF solution to solid clathrate at ambient pressure and slightly below the freezing point of 277 K itself takes a time period of close to about 20 min to 1 h.[25,42] [In some studies even longer time period of 170 min (Ref. 43) has been used or else the solution has been left overnight at 275 K for forming the clathrate.[12]] Therefore, one would expect a much slower kinetics of clathrate formation at 130 K during depressurization in this study than on keeping isothermally at 275–277 K. Consequently, the number of clathrate crystals formed over a given time period would be lesser, their size smaller, and their perfection less than those of the crystals formed on cooling and annealing at 275–277 K. In this context, we recall that the pressure for the collapse of ice Ih has been found to depend upon its microstructure, i.e., crystal size, defects, etc.,[41,44] being higher for the usual (larger size) polycrystalline ice Ih and lower for microcrystalline ice Ih. Since the collapse of such crystals formed at high temperature in this study occurs at a somewhat higher pressures than for those formed at 130 K [Figs. 3 and 4(a)] as for microcrystalline ice Ih, our results show that this is the case also for the clathrate.

The solution's viscosity at the p and T before the clathrate formation is of the order of centipoises and hence the molecular diffusion rate is high. If the clathrate formation in the solution is a rate-controlled process as in a chemical reaction kinetics, it would mean that this kinetics is already very slow in the low viscosity solution. It would be slower at higher p and lower T. This would also explain the earlier findings that the original state could not be easily recovered on depressurization of the collapsed state at low temperatures, unless the pressure was completely released. For example, Handa *et al.*[13] found that when p was decreased from 1.72 GPa to 70 MPa in 10 min and the sample recovered at 77 K at ambient pressure, a rapid transformation occurred during the recovery of the sample on unloading and its state reverted to the original clathrate. However, on *in situ* heating from 77 to 119 K at 70 MPa the sample recovered 70% of its initial volume, and when heated from 77 to 129 K at 210 MPa, it recovered 85% of the initial volume. Thus transformation at 1.3 GPa produced a phase that could neither be recovered at 77 K after depressurizing directly to ambient pressure nor did it fully revert at T below 130 K and $p > 0.07$ GPa.[13]

Some information on whether the original clathrate can be fully recovered on depressurizing or not may be obtained by heating of the state formed after pressure cycling twice in the range 0.05–1.3 GPa at 130 K, as plotted in Fig. 4(b). Here, the κ values for the as-made clathrate were recovered after an apparent phase transition that occurred in the temperature range of 138–144 K. The recovery of this phase at a higher T indicates that molecular diffusion rate at 130 K and 0.05 GPa is too slow to allow full reversion to the original clathrate structure, and this rate is sensitive enough to T that the original state is recovered by raising T only by 8–14 K. Alternatively, the state formed on depressurization to $p < 0.35$ GPa at 130 K may be an intermediate, lower density structure, possibly amorphous. An analogous state is that of the low-density amorph of ice which is obtained by heating the pressure-collapsed ice Ih to ∼135 K at 100 bar.[45] This low-density amorph transforms to the original cubic ice and ice Ih on heating at ambient pressure or reverts to HDA on repressurizing.[45] It seems that detailed studies by *in situ* x-ray or neutron diffraction may be needed to further investigate this issue.

V. CONCLUSION

THF ice clathrate at 130 K begins to collapse at a pressure near 0.75 GPa. Its κ first tends become constant and then decreases indicating that the decrease in the phonon mean-free path has the dominant effect. It then increases as the increase in the density and sound velocity becomes dominant. When the initial minimum and ultimate rise in κ are considered there is an overall increase in κ by ∼10%. The collapse of ice Ih continuously decreases κ.[22] In this respect, therefore, the characteristic feature of the pressure collapse of clathrate differs from that of ice Ih. Although the pressure collapse progresses according to the first-order kinetics for both at a fixed T and p, the rate is much faster for the clathrate than for ice Ih.

In view of recent *ex situ* x-ray diffraction data and *in situ* Raman data,[14] we conclude that the THF clathrate hydrate begins to amorphize at ∼0.75 GPa at 130 K. Rapid increase in the density and κ occurs at p of about 1.05 GPa, and the amorphization is complete at ∼1.25 GPa. The ∼10% increase in κ on amorphization is attributed to the strong density increase that increases κ despite the crystalline to amorphous transformation.

Depressurizing the amorphous state slowly at 130 K does not allow recovery of the original structure at 0.05 GPa. A temperature increase to 138 K or higher at 0.05 GPa allows it. The denser, collapsed state of the clathrate transforms in a two-step manner to a structure whose κ is identical to that of the original clathrate. It is suggested that the intermediate state would also be a disordered state.

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