

On the Unusual Thermal Conductivity of Ices at Elevated Pressures

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Almost all the numerous forms of ice including 13 crystalline phases, several distinct amorphous states as well as clathrate hydrates have been characterized in terms of their thermal conductivity κ . A few deviations from both the typically strongly decreasing $\kappa(T)$ ($\kappa \sim T^{-1}$) associated with crystals and the weakly increasing $\kappa(T)$ associated with glassy states are observed. In particular, the crystalline clathrate hydrates show glass-like κ , whereas low-density amorphous (LDA) ice shows crystal-like κ ($\kappa \sim T^{-0.6}$). The latter is unique for an amorphous state and indicates that LDA ice exhibits a surprisingly high degree of structural order that allows for high-frequency phonon propagation. It also implies that LDA ice is not the glassy counterpart of ambient liquid water that shows typical amorphous-like behavior. Moreover, the crystalline ices Ih and Ic and LDA ice exhibit abnormal negative pressure coefficients of κ . Both ices Ih and Ic demonstrate pressure-induced amorphization to high-density amorphous (HDA) ice, a state to which also LDA ice transforms on pressurization. The negative pressure coefficient is a signature of phonon softening which leads to a disordering transition upon pressurization.

Introduction

There are numerous forms of ice including 13 crystalline phases,¹⁾ several distinctly different amorphous solid states and various clathrate hydrates. Ten of the crystalline phases, namely, ices II, III, IV, V, VI, VII, VIII, IX, X and XII, are produced at high pressures and three, hexagonal (Ih) and cubic (Ic) ices and ice XI, are produced at ambient pressure. The amorphous forms of solid water are: (i) amorphous solid water formed by hyperquenching micron-sized droplets (HQW) and by vapor-deposition on a cold plate (ASW),¹⁾ (ii) high-density amorphous ice,²⁾ (iii) low-density amorphous ice³⁾ and (iv) very high-density amorphous ice.⁴⁾

While all the crystalline phases of water have been unequivocally established and the similarity between ASW and HQW is reasonably well established, the distinction between the amorphous states produced at high pressures and their relation to ASW is not. One of these amorphous states is formed by subjecting ice Ih or ice Ic at 77 K to a pressure of ~ 1.5 GPa.²⁾ Its density of 1.17 g cm⁻³ at 77 K and 0.1 MPa is higher than that of ASW (0.94 g cm $^{-3}$), and therefore it has been called high-density amorphous (HDA) ice. The second, low-density amorphous (LDA) ice, is formed by heating HDA at ambient pressure from 77 K to 125 K.³⁾ The HDA ice can be densified further by heating from 77 K to 160 K at pressures near 1 GPa, instead of 0.1 MPa.⁴⁾ The solid recovered at 77 K and 0.1 MPa has a density of 1.25 g cm $^{-3}$ and is designated as very high-density amorphous (VHDA) ice.

Although LDA and ASW (HQW) have the same density and show radial distribution functions and structure factors that are nearly identical,⁵⁾ these states also exhibit distinct differences, *e.g.* in results of inelastic neutron scattering.^{6,7)} In this respect, LDA shows a closer relationship with crystalline ices than with ASW and, as shown here, the thermal conductivity of LDA also displays a striking similarity to those of crystalline phases. These results provide evidences for that ASW and LDA are not identical states even though this is occasionally implied. In the case of VHDA and HDA, the situation is the opposite. VHDA was initially reported to be yet another distinct solid amorphous state of ice. However,

© 2005 The Japan Society of Calorimetry and Thermal Analysis. 232 Netsu Sokutei 32 (5) 2005 new findings indicate that the state is better described as a densified, relaxed, state of HDA.^{8,9)} These results also show that the measured properties of HDA can be significantly dependent on thermal history - much more than for glassy liquids in general. Therefore, the HDA states produced at 77 and 130 K are here denoted HDA_{77K} and HDA_{130K} where these need to be distinguished. The original notation VHDA is, however, kept for the amorphous state formed by heating HDA at 1 GPa to above 150 K.

The nature of the HDA to LDA transition is also not established. On warming at ambient pressure the transition from HDA to LDA occurs via multiple distinct states¹⁰⁾ - indicating that several states between LDA and HDA can be produced, whereas a first-order transition is reported in a recent high-pressure study.¹¹⁾

In addition to the various pure ice states, ice can form clathrate hydrates under the coexistence with hydrophobic substances. The host water molecules form several kinds of Archimedian polyhedral cages through hydrogen bonds, and the cages accommodate guest species which stabilize the lattice. Examples of guest molecules are: tetrahydrofuran, 1,3-dioxolane, and many that are gases under normal conditions (e.g. CO₂, CH₄, Xe). Clathrate hydrates have attracted considerable interest during the last decades because of many potential applications. For example, methane trapped in clathrate hydrate may represent the largest source of hydrocarbons on earth. Besides the potential of becoming an important source for energy systems, clathrate hydrates have been suggested for use in deep sea deposition of CO2 and for storage of H₂.¹²⁾ The surprising finding of low and "glass-like" thermal conductivity13) (positive temperature coefficient) for all clathrate hydrates has also encouraged the search for improved materials for use in thermoelectric applications.

One of few properties that have been reported for almost all the various forms of ice is the thermal conductivity. The thermal conductivity κ of well-ordered simple crystals generally varies as $\kappa \sim T^{-1}$ at temperatures of order and above the Debye temperature. This can be understood in terms of the simple Debye formula for κ , which is given by:¹⁴⁾

$$\kappa = (1/3) \rho C v^2 \tau \tag{1}$$

where ρ is the mass density, C is the specific heat capacity, v is the phonon velocity and τ is the time between scattering events. At high temperatures, the main source for phonon scattering is three-phonon Umklapp processes. Since the number of phonons increases proportionally to temperature, the probability for scattering events increases and τ varies as T^{-1} , which is also reflected in $\kappa(T)$. Slight deviations from the T^{-1} dependence are, however, commonly observed. A somewhat stronger temperature dependence than $\kappa \sim$ T^{-1} can be due to influence by higher-order phonon processes and/or the thermal expansion, whereas a weaker dependence is commonly due to scattering arising from structural disorder. In the case of an amorphous state, the disordered structure does not allow for long-range phonon propagation, at least not for high-frequency excitations. In terms of Eq.1, this is described by a very short and constant τ , which yields a roughly constant $\kappa(T)$. A constant or even increasing κ with increasing temperature is therefore associated with glass-like behavior, whereas a strongly decreasing κ is associated with crystal-like behavior. Only a few exceptions to these generalizations have been reported and ice exhibits two of those states. The LDA ice displays unique crystallike κ ,¹⁵⁾ which has not been found before for an amorphous state and, as mentioned above, the crystalline clathrate hydrates all show glass-like behavior.¹⁶⁾

Generally, κ increases with increasing pressure due to the associated increase of the phonon velocity and decrease of the lattice anharmonicity. The latter decreases the scattering rate and therefore τ increases. However, also in this case ice shows deviations. Both the crystalline ices Ih and Ic as well as LDA ice show a decreasing κ , which can be attributed to softening of lattice modes that on further pressure increase may lead to amorphization.¹⁷⁾ The softening of the modes decreases the phonon velocity and increases the anharmonicity, which both favor a decreasing κ (See Eq.1).

In this review the results for the temperature and pressure behaviors of κ for the various forms of ice are summarized and discussed. In particular, the deviations from the almost universal behaviors of κ for glassy liquids and crystals along with their implication on pressure-induced amorphization and phase interrelations are discussed.

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Experimental technique

All the, *in situ*, high-pressure studies of κ for ice have been done using the transient hot-wire method. An outline of the method is that a Ni-wire (0.1 mm in diameter), *i.e.* the hot-wire probe, is placed in a ring of constant radius within a Teflon cell. The probe is surrounded by the medium under investigation and heated by a 1.4 s long pulse of about constant power. The resulting temperature variation is monitored by measuring the electrical resistance between two potential taps. A theoretical expression for the temperature rise is fitted to the data points thereby yielding κ and, with lesser accuracy, also the heat capacity per unit volume. The inaccuracy in κ is less than ± 4 %.

The Teflon cell is mounted in a piston-cylinder type of apparatus of 45 mm internal diameter and the whole assembly is transferred to a hydraulic press that supplies the load. Temperature is varied by heating or cooling the whole vessel using a built-in refrigerator, and measured by a Chromel versus Alumel thermocouple. Pressure is determined from the load/area with an empirical correction for friction.

Low temperature phase behavior and pressure-induced amorphization

Fig.1 shows κ upon pressurization of ices Ih and Ic at 130 K. At about 0.8 and 0.7 GPa, κ decreases abruptly due to the collapse of the ice lattice. The significant decrease of κ reflects the change from the crystalline phase with long-range phonon propagation to the amorphous state in which high-frequency phonons cannot propagate. In absence of crystallization in the transformation range, the final state produced is highdensity amorphous ice HDA_{130K}. Since it is produced by isothermal pressurization of ice Ih (or ice Ic) at temperatures near 130 K, it should be a state with density in between that of HDA_{77K} and VHDA. On isobaric heating at 1 GPa, HDA_{77K} is densified progressively in the whole temperature range up to 165 K, and has been densified about half way to that of VHDA at 130 K.⁴)

A subsequent isothermal depressurization of HDA_{130K}, induces a transition to LDA at ~ 0.05 GPa and, as can be seen in **Fig.1**, κ increases abruptly at the transition. This indicates that the order increases significantly at the HDA to LDA transition, which agrees



Fig.1 Thermal conductivity as a function of pressure at 130 K during successful amorphization of ices Ih and Ic () and during two runs which are interrupted by sudden crystallization to metastable ice/ice XII (see text) shown by the arrows (,). Results for metastable ice/ice XII immediately after the sudden crystallization () and the subsequent depressurization or pressurization (). Results on depressurization of HDA_{130K}, which undergoes a transition to LDA ice () or slow crystallization (dashed line).

with a deduction from entropy calculations for the two amorphous states.¹⁸⁾ LDA ice transforms back to HDA ice at ~0.4 GPa on pressurization (Fig.1). It is believed that the pressure hysteresis observed in the transformations between the two states is due to the sluggishness at low temperatures and it has been suggested that the states are in thermodynamic equilibrium at about 0.2 GPa at 130 K. The extension of the suggested equilibrium line between HDA and LDA to higher temperatures provides the main argument for the existence of two liquid states of water, and a second critical point. The liquid counterpart of LDA cannot, however, be regarded as established since clear glass transitions features are lacking in most experimental data.¹⁹⁾ Although this is also the case for HDA ice, recent findings indicates that this state does exhibit a glass transition^{20,21} and that it is almost independent of pressure.21)

The production of the HDA and LDA states is not always straightforward. Quite frequently (~80 % of the runs), the sample crystallizes after the transformation into HDA_{130K} has commenced. The phase formed at the crystallization has not been investigated by X-ray diffraction, but it is known that ice XII can be produced at these p,T-coordinates. Ice XII was established in 1998, when it was formed through a rather special procedure.²²⁾ D₂O water crystallized into this new structure when containing 6-10 mass% SiO2 wool and cooled slowly to 260 K at 0.55 GPa. It is now known²³⁾ that ice XII can be produced by isothermal pressurization of ice Ih below ~ 150 K, and that it was accidentally produced in earlier studies of HDA ice. It also forms reproducibly when HDA at ~0.8-1.2 GPa is heated from 77 K to ~180 K at 15 K min⁻¹ rate or higher.^{8,24)} In studies of κ ,²⁵⁾ an ice phase was formed on pressurization of ice Ih at ~ 130 K yielding a discontinuous change in κ (see arrows in Fig.1) at the same time as the sample volume decreased abruptly. But it is not certain that the phase formed is ice XII since it is believed to form as a result of a shockwave, which is caused by a sudden release of a jammed piston.²⁶⁾ That is, the unjamming of the piston causes the transition, which was not the situation in the investigation of κ .²⁵⁾ Moreover, there is also a report that ice XII forms only from HDA and not from ice Ih.27) Neither this was the case in the study of κ ,²⁵⁾ where repeated tests showed that the transition could occur anywhere in the amorphization range ($\sim 0.8-1.2$ GPa). Since a sample that transformed in the beginning of the amorphization range exhibited the same κ as a sample that transformed at the middle or end of the range (see Fig.1), to within the experimental inaccuracy, this precludes that only the HDA parts of the sample did transform. Consequently, further detailed investigations using in situ X-ray measurements are needed to certify whether or not the produced phase in the study of κ is ice XII and, therefore, the phase is here given the notation metastable ice/ice XII.

The production of LDA is complicated by the tendency of slow crystallization of amorphous ice. A slow depressurization procedure necessary for the κ measurements can therefore induce a transformation to ice Ic/Ih instead of a rapid transformation to LDA. An example of this is shown in **Fig.1** as a dashed line. Here the sample starts to crystallize slowly near 0.2 GPa during depressurization at ~122 K. The transformation back to HDA at a pressure above 0.7 GPa proves that some amount of ice Ic/Ih had formed instead of LDA ice. The reason for this can be nucleation and growth of ice Ic but also that some small crystals might have survived during the amorphization process and starts to



Fig.2 Thermal conductivity for the crystalline ices, amorphous ices and tetrahydrofuran clathrate hydrate doped with 1.8×10^{-4} mole fraction of KOH against H₂O. The arrows show the step at the phase transition of THF clathrate hydrate and at the XI to Ih transition, which are due to proton disordering. The dashed line shows the typical behavior for crystalline phases: $\kappa \sim T^{-1}$.

grow at low pressures. It is, however, straightforward to check whether or not pure LDA has been produced by pressurization to above 0.4 GPa at 130 K to obtain HDA ice again. Even a minute amount of crystals will cause κ to exceed that of the original HDA ice.

Thermal conductivity of crystalline ices and clathrate hydrates

The isobaric results for the crystalline phases of ice are shown in Fig.2. The only phases that have not been investigated are ices IV, X, and perhaps ice XII. As mentioned, three of the thirteen crystalline phases of ice can be produced at atmospheric pressure: ices Ih, Ic and XI, but ice Ih is the only phase for which the atmospheric κ has been determined by direct measurement. The results of the numerous investigations of Ih have been evaluated by Slack,28) who also provided best estimate values for κ in the range 10-273 K. The more recent results for ice Ih, calculated from measurements at elevated pressures,29) agree to within 3 % with the best estimate values. Ice XI, which is essentially a proton-ordered form of Ih, is obtained by cooling ice Ih to below 72 K. However, the transition is too slow to be observed unless the ice rules30) are relaxed by doping the sample, e.g. with a minute amount

of alkali hydroxides, particularly KOH (~ 10^{-4} mole fraction). The dopant introduces lattice defects, which reduce the severe restriction imposed to the cooperative nature of the water reorientational motion and therefore accelerates the proton ordering process. Still the transition is sluggish and it is therefore not possible to obtain more than about 70 % of ice XI in a laboratory time. This situation needs to be taken into account when properties of ice XI are measured and discussed. Ice Ic can be produced at atmospheric pressure by heating of ASW, but it is difficult to obtain pure bulk samples since ice Ic tends to coexist with ice Ih. A high-pressure route for obtaining ice Ic was used in the studies of κ for ice Ic: ice II transforms to almost pure ice Ic on warming at low pressures.

As can be seen in Fig.2, the phases can be clearly distinguished by the magnitude and/or temperature behavior for κ . That is, κ provides a kind of fingerprint for each phase. Although the temperature dependence for κ of some phases is somewhat weaker than that expected from Eq.1 ($\kappa \sim T^{-1}$, which is shown as a dashed line in Fig.2), κ is invariably strongly decreasing with increasing temperature, *i.e.* all crystalline ice phases show typical crystal-like behavior. It is common also that high-pressure phases exhibit higher values for κ than low-pressure phases. However, this is not a general rule for the ice phases. The ambient pressure phases: ices Ih, XI and ice Ic exhibit higher values than most of the other ice phases. Ices VII and VIII are exceptions, but these consist of two interpenetrating ice lattices. It is apparent that the structures of the ambient pressure ice phases, having a strongly hydrogen-bonded network with short nearest neighbor distances - shorter than the high-pressure phases, are favorable for heat conduction.

The newly observed metastable ice/ice XII exhibits the lowest κ among the crystalline ices, which are metastable at low temperatures. The temperature dependence is rather low ($\kappa \sim T^{-0.6}$), which is an indication of structural disorder. Ice XII is believed to be fully proton disordered, but proton disorder alone cannot explain the low values for κ of this phase since the proton disordered ices Ih and Ic have significantly higher κ . It is reasonable to assume that the production process of this phase with two different states present at the transition (HDA and ice Ih) is unfavorable for obtaining good crystals. Since the phase formed at the transition has almost the same κ irrespectively if it is formed from mainly ice Ih or mainly HDA_{130K}, it seems unlikely that the phase would be a mixture. However, it cannot be ruled out that a mixture of a fixed amount of two different phases is always produced at the transition. In that case, it would most likely consist of ices XII and another crystalline phase.

Since several ice phases exhibit a proton-ordering transition, it is possible to make some conclusions about its effect on phonon propagation. One interesting observation is that it does not seem to significantly affect the temperature dependence, as shown by the almost identical behaviors of $\kappa(T)$ for ices Ih and XI. However, the magnitude for κ decreases about 22 % at the protondisordering transition from ice XI to ice Ih. A similar decrease (25 %) is found at the transition between ices IX and III, whereas 40 % differ between ices VIII and VII.^{31,32)} Upon cooling, ice III transforms to ice IX in which the water molecules order in an antiferroelectric way. The larger decrease in κ at the VIII -VII transition than for the lower pressure phases could possibly be associated with the two interpenetrating Ic substructures of both phases.

Clathrate hydrates exhibit much different temperature behavior than the crystalline ices. Although the clathrate hydrates have a well-ordered crystal lattice, the behavior of κ is similar to those of glassy liquids. That is, κ increases with increasing temperature, as shown in Fig.2 by the results for tetrahydrofuran (THF) clathrate hydrate, doped with 1.8×10^{-4} mole fraction of KOH against H₂O.³³⁾ All clathrate hydrates show a weakly increasing $\kappa(T)$ with a magnitude which is only weakly dependent on the type of guest molecule.34) The magnitude for κ is much lower than those of crystalline ices, and also lower than that for HDA ice. Although the reason for this glass-like behavior is perhaps not fully established, the most reasonable explanation is given by the resonance scattering model.35,36) In this model, strong phonon scattering is caused by interactions between the encaged molecules and phonons.

Clathrate hydrates exhibit proton disorder at high temperatures, but can become ordered through a firstorder transition at low temperatures - in a manner similar to ice Ih. Again the transition is sluggish and, as for the ice Ih to ice XI transition, it must be promoted by using a dopant to relax the ice rules. This was first shown in a study of KOH-doped THF clathrate hydrate where the dopant induced a transition at 62 K at atmospheric pressure.37) In addition to proton ordering, it was suggested37) that the guest molecules become ordered since no dielectric dispersion has been observed below this transition. A local electric field produced by the proton ordering in the host lattice will force the guest THF molecules to align along a preferred direction in the low temperature phase. The transition can also be detected in the results for κ as the magnitude of κ changes (~15 %) (Fig.2). However, the glass-like temperature behavior remains unaffected. Together with the results for the ice phases, e.g. ices Ih and XI, this indicates that proton disorder affects mainly the scattering strength and not the scattering source. That is, the same scattering source is dominant above as below the transition. In crystalline ices, three-phonon Umklapp scattering is dominant and responsible for the $\kappa \sim T^{-1}$ dependence, whereas resonance scattering caused by guest and host interactions is a strong candidate for the glass-like κ of clathrate hydrates. The increase in magnitude of κ is accounted for by a decrease of the phonon-phonon or phonon-guest coupling via a decrease in the lattice anharmonicity at the ordering transition.

The pressure dependence of κ for the various ices is shown in Fig.3. The thermal conductivity of phases generally increases with increasing pressure irrespectively of the structure, with only a few exceptions. As can be seen in Fig.3, all crystalline ices except ices Ih and Ic, follow this rule. The almost invariably observed increase is due to increasing phonon velocity and, probably, decreasing phonon scattering (decreasing anharmonicity) with increasing pressure. The decrease of κ for the ices Ih and Ic can therefore be attributed to the unusual feature of a pressure-induced decrease of the phonon velocity. This has been verified for the transverse sound velocity of ice Ih.38) This softening of the transverse modes eventually leads to instability of the lattice and collapse into HDA ice near 1 GPa. Another characteristic of phases that have shown pressure-induced amorphization is negative thermal expansivity at low temperatures. Both this and the negative pressure coefficient of κ , have the same origin-negative Grüneisen parameters.¹⁷⁾ On the basis of these findings one can conclude that a phase that has a positive pressure coefficient of κ will unlikely be amorphized upon pressurization. Consequently, no



Fig.3 Thermal conductivity for crystalline and amorphous ices plotted against pressure. Most phases show positive pressure coefficient of κ but ices Ih, Ic and LDA ice are exceptions, and these three states all undergo disordering transitions to HDA (or VHDA) ice upon pressurization.

other crystalline phases of ice have this ability except perhaps ice XI. In this case, the results for κ are obtained in a limited pressure range and at quite low temperatures (58 K), which makes a conclusion based on the pressure coefficient of κ somewhat uncertain.

Thermal conductivity of amorphous ices

The isobaric thermal conductivity of the amorphous ices is shown in Fig.2. The results for HDA are typical glass-like and indicate an interrelationship between HDA and liquid water. The thermal conductivities of all glassy liquids are connected smoothly to those of the corresponding liquids. That is, there has never been any observation of a discontinuous change in κ at the glass transition temperature $T_{\rm g}$, as is normally the case at the first-order transitions. Instead $d\kappa/dT$ may change slightly from typically being weakly positive below $T_{\rm g}$ to weakly negative above $T_{\rm g}$. The change in the slope is explained well by the increase in the thermal expansivity at $T_{\rm g}$ and the correspondingly stronger decrease in density above T_g than below. Since κ (normally) decreases with decreasing density, this causes a weak decrease in the temperature coefficient of κ . But as can be seen in Fig.2, $d\kappa/dT$ for liquid water is even larger than that for HDA_{130K} ice and the magnitude would be somewhat smaller than that for HDA_{130K} at similar temperatures. The former is

explained partly by the abnormal negative thermal expansion of liquid water below 4 at 1 atm and partly by delocalized librational modes which contribute increasingly to κ with increasing temperature.³⁹⁾ Since the thermal expansivity of liquid water becomes positive at higher pressures and the librational modes would not be excited at low temperatures, it is likely that the change in $d\kappa/dT$ at a hypothetical liquid water to HDA transition at high pressure would be similar to that normally observed at glass transitions. The difference in magnitude at 1 atm can be explained by the difference in density. Liquid water at ambient pressure has lower density than HDA_{77K} ice (1 g cm $^{-3}$ and 1.17 g cm $^{-3}$, respectively) and the density of HDA130K is yet slightly larger. Considering the results for κ alone, HDA (or rather VHDA) is therefore a good candidate for the hypothetical glassy state of pressurized liquid water. The state will be realized if liquid water is pressurized to 1 GPa and thereafter cooled rapidly from the liquid state down to low temperatures. The hot-wire method normally yield an anomalously small peak in κ at a glass transition, as a result of a time dependence in the heat capacity, but the data do not show any indication of that. Consequently, either there is no glass transition before the sample transforms to LDA ice or the heat capacity jump at $T_{\rm g}$ is too small to be observed with the hotwire method. A dielectric study of HDA130K at high pressures,²¹⁾ where the transition to LDA ice is avoided, shows a relaxation process with a relaxation time near 1 s at 140 K. This indicates that the state is an ultraviscous liquid under these conditions, which would confirm the liquid counterpart of the high-density amorphous ice.

The results for κ of LDA ice are strikingly different from that expected for an amorphous state. In fact, these are similar to those of crystalline phases. The temperature dependence is $\kappa \sim T^{-0.6}$, which is almost the same as that for ices V and VI.³²) Moreover the magnitude for κ is almost as large as for ice III (**Fig.2**). The results for LDA ice are typical for a state in which both structural disorder and three-phonon Umklapp scattering is limiting phonon propagation, but where the latter is the main source for phonon scattering. The behavior is unique in that the state would be characterized as a crystalline phase as far as the thermal conductivity is concerned. However, all structural data provide evidence for an amorphous state. The crystal-like κ of LDA also seems to preclude a possibility that liquid water at normal pressure is the liquid counterpart of LDA ice. This should be a requirement in the two-liquid model unless there is a liquid-liquid transition on cooling at 1 atm. If the hypothetical phase line between two liquids extends to negative pressures⁴⁰⁾ then there would indeed be a liquidliquid transition on cooling that cannot be observed due to crystallization in this temperature range. Quenching of liquid water to avoid crystallization and obtain ASW (or HQW) would yield a low-pressure (density) version of HDA ice as the liquid-liquid transition is probably also circumvented. In such a scenario, the two-liquid model could still be correct. Another remote possibility is that the glassy state of ambient liquid water exhibits crystal-like phonon properties, which should then be associated with the (low-frequency) transverse modes that can propagate in the solid state but not in the liquid state. Such behavior has never been observed and the possibility could be excluded if κ of bulk ASW is determined. The thermal conductivity of porous ASW has invariably been found glass-like but with a magnitude which depends on the production conditions.41) Direct measurement of κ for bulk ASW is desirable but hampered by experimental difficulties.

The pressure dependence for κ of the amorphous ices is shown in **Fig.3**. HDA ice shows normal behavior with a positive pressure coefficient of κ , in agreement with that for liquid water at room temperature, whereas the behavior of LDA ice is abnormal. A pressure-induced decrease of κ is unusual for crystals, ice Ih and Ic are two of few exceptions, and has never before been observed for an amorphous state. The crystalline ices Ih and Ic exhibit phonon softening and undergo amorphization to HDA at higher pressures, in agreement with the behavior for LDA ice. One can conclude that LDA ice also in this respect is crystal-like and exhibits pressure-induced phonon softening, which yields HDA ice via a disordering process.

Conclusions

Several of the modifications of ice exhibit unusual behavior for κ such as crystal-like behavior for an amorphous state (LDA ice) and glass-like behavior for a crystal (clathrate hydrates) as well as pressure-induced decrease of κ (ice Ih, ice Ic and LDA ice). These unusual results provide information on both the interrelations

between phases and pressure-induced structural instability, which may result in amorphization. Consequently, water exhibits many unusual properties also in the solid states.

In particular, the crystal-like behavior for κ of LDA ice, i.e. strongly decreasing κ with increasing temperature, does not corroborate the suggestion that liquid water is the liquid counterpart of LDA ice. In fact, this result for LDA ice indicates a stronger relation to crystalline phases than amorphous states, which provides negative evidence for the two-liquid model in which a second critical point exists at positive pressures. But the glasslike behavior and the magnitude of κ similar to that of liquid water substantiate a hypothesis that HDA is the glassy counterpart of pressurized liquid water.

The unusual negative pressure coefficient of κ for the ices Ih and Ic is due to phonon softening and the associated decrease of the phonon velocity. In the cases of ices Ih and Ic, this phonon softening leads to amorphization at high pressure if crystallization to another ice phase is avoided. The unusual negative pressure coefficient of κ is therefore a signature of pressure-induced amorphization. Consequently, phases that exhibit increasing κ with pressure will unlikely undergo pressure-induced amorphization. This is the case for ice XI, the proton ordered phase of ice Ih.

LDA ice exhibits negative pressure coefficient of κ , which has not been observed before for an amorphous state. This further demonstrates the crystal-like behavior of LDA ice and its deviation from liquid water possessing positive pressure coefficient of κ at room temperature. The lack of interrelationship between LDA ice and ambient liquid water, which is displayed in the results for κ shown here, can be established by a study of κ for bulk ASW.

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