PHYSICAL REVIEW B **74**, 184201 (2006)

Dielectric properties of high-density amorphous ice under pressure

Ove Andersson[1,2,*] and Akira Inaba[2,†]
[1]*Department of Physics, Umeå University, 901 87 Umeå, Sweden*
[2]*Research Center for Molecular Thermodynamics, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan*

(Received 6 July 2006; revised manuscript received 20 August 2006; published 1 November 2006)

The dielectric properties of high density amorphous ice, which is produced by slow isothermal pressurization ($\sim$0.1 GPa h^{-1}) at 130 K, have been studied by dielectric spectroscopy, *in situ*, at pressures up to 1.2 GPa and temperatures from 130–160 K. The dielectric relaxation time τ is about 5 s at 130 K and follows an Arrhenius temperature dependence with an activation energy E_a=45 kJ mol^{-1} at 1 GPa. The short τ indicates that the amorph at 1 GPa is an ultraviscous liquid well before it crystallizes at $\sim$160 K. The equilibrium permittivity is $\sim$157 at 138 K and 1 GPa, which yields a Kirkwood correlation factor g_K of only 1.7, indicating a much smaller dipolar orientational correlation than that of the stable crystalline phase ice VI (g_K=3.4) and liquid water at atmospheric pressure (g_K=2.9 at 273 K). The activation volume is 1.7 cm^3 mol^{-1} in the pressure range 0.45 to 1.15 GPa at 130 K which, together with E_a, yields a weak pressure dependence of the glass transition temperature T_g of dT_g/dp=5 K GPa^{-1}.

DOI: 10.1103/PhysRevB.74.184201 PACS number(s): 64.70.Pf, 77.22.Gm, 62.50.+p

I. INTRODUCTION

One of the more remarkable findings in the behavior of water, among its many unusual features, is that it exists in several different amorphous solid forms. Some of these are produced at low temperatures through a pressure induced collapse of the hexagonal or cubic ices. Isothermal pressurization at 77 K, yields a high density state at 1.2 GPa that has typical amorphous diffraction pattern,[1] and has been referred to as the high-density amorph (HDA). This state transforms further to a low-density amorphous (LDA) form[2] on isobaric heating at pressures below 0.07 GPa up to $\sim$130 K.[3] During heating of HDA at high pressures above $\sim$0.5 GPa,[4] it densifies before crystallization, and the ultimate densified form has been referred to as very HDA (vHDA)[5] or relaxed HDA (rHDA), where the latter notation is suggested for a state produced by isobaric heating of HDA below 0.8 GPa.[6]

However, a recent study indicates now that HDA produced at and near 77 K is not a well-defined homogeneous solid, and only after HDA has been heated under pressure to yield vHDA does it become homogeneous.[7] The sluggish kinetics at low temperatures may thus restrict the ultimate collapse of hexagonal ice (ice Ih) to a homogeneous amorph. The various HDAs obtained at different (low) temperatures, pressures, or obtained by using different pressurization and depressurization rates, sample size, annealing time, etc., can therefore have yielded heterogeneous solids with slightly different diffraction patterns and densities. Previously reported results of the amorphs should now be considered in the light of these findings.

The structure of the amorphous states produced under pressure has been studied in several recent investigations,[8–12] but the conclusions have been subject to interpretations of the diffraction data. All the amorphous states appear to consist of tetrahedrally coordinated fully hydrogen bonded networks but one important distinguishing feature is found in the nearest neighbor oxygen-oxygen coordination, and it concerns interstitial nonhydrogen bonded molecules.[8,9] At atmospheric pressure, the HDA state produced by pressurization at 77 K has roughly one (interstitial) nonhydrogen bonded molecule and vHDA about two molecules in the first neighbor shell,[8] whereas the LDA state exhibits no such interstitial molecules. Klotz *et al.*[10] have discussed their results for HDA ice in terms of increasing interpenetrating hydrogen networks with increasing pressure, but Martonak *et al.*[13] have argued that it is incompatible with their results of molecular dynamics simulations of HDA and vHDA ice.

The structure of LDA ice shows local order similarities with ice Ih, with a nearest neighbor coordination which is close to four. Still the LDA state shows typical amorphous x-ray patterns. The distinction between the LDA and HDA states becomes further obvious in terms of their phonon properties.[14–17] The LDA state shows crystal-like thermal conductivity, i.e., the phonon scattering is apparently dominated by three phonon umklapp scattering, whereas the HDA exhibits glasslike thermal conductivity.[14,18] The behavior of the LDA state is unique in that the state would be characterized as a crystalline phase as far as the thermal conductivity is concerned. Also results for inelastic x-ray scattering show phonon propagation up to unusually high frequencies.[15] In fact, this is the case for both the HDA and LDA states, but it is much more pronounced in the LDA state.

Some results suggest that the transition from HDA to LDA occurs via multiple distinct states on warming at ambient pressure[11]—indicating that several states between LDA and HDA can be produced. This result differs from one obtained in an *in situ* high-pressure study, which reports a first-order transition between LDA and HDA.[12] The distinction between these two cases is important since the latter provides support for the two liquid models of water, where the LDA and HDA (or rather vHDA/rHDA) states are the corresponding two glassy liquids. Although the model is not disproved, it is more difficult to reconcile the model with a multiplicity of distinct amorphous solid states. Moreover, together with the findings for the production of densified HDA, where vHDA is the ultimate density form, this means that it might be possible to produce numerous amorphous states with different densities between those of LDA and vHDA, which are

©2006 The American Physical Society

$0.94\ \mathrm{g\,cm^{-3}}$ and $1.25\ \mathrm{g\,cm^{-3}}$, respectively, at atmospheric pressure.

In the case of vHDA/HDA, the transformation from HDA to vHDA has been found to be gradual so here it is particularly important to provide the detailed thermal history to declare the state of the sample. Lately this has been taken into account by various labeling of the state of the high density amorph such as vHDA and rHDA. Previously, all amorphous ices produced by pressurizing Ih to above 1.2 GPa at low temperatures in the range 77–140 K have been denoted HDA. But since HDA produced at 77 K densifies irreversibly on heating at 1 GPa, the density as well as other properties become slightly different if the state is produced at higher temperatures and at slower pressurizing rates. These differences are reflected in different transformation temperatures for the HDA to LDA transition on heating at low pressures.[7,19] HDA samples produced, or annealed, at high temperatures acquire higher density and are thermally more stable than low-temperature samples, which yields higher transformation temperatures to LDA. The measured properties of the high density amorph seem therefore to be significantly dependent on thermal history—much more than for glassy liquids formed by using different cooling rates.

Many important issues remain to be established concerning the low temperature behavior of solid water. These are ultimately important for understanding the many unusual behaviors of liquid water such as the increase of the heat capacity and decrease of density on increasing supercooling of liquid water. The two-liquid model and an associated second critical point is one of the models that provide an explanation for the behaviors of supercooled liquid water. A key issue for establishing or refuting the two-liquid model is the understanding of the nature of the amorphous solid states. In addition to the pressure produced amorphous states, amorphous solid water can also be produced by vapor deposition onto a cold plate (ASW) and by hyperquenching micron-sized liquid water (HQW). It has been shown that after heating of ASW from 77 K to 113 K in vacuum (annealed ASW), the resulting state is indistinguishable from HQW[20,21] and, consequently, that annealed ASW and HQW are most likely identical states. However, the interrelations between the other amorphous solid states are disputed. LDA is sometimes assumed to be the same state as ASW but these states exhibit significant differences in neutron scattering results,[16,17] and most likely also in thermal conductivity behavior, which is crystal-like for LDA ice.[14,18] The crystal-like properties of LDA seem to preclude that liquid water at normal pressure is the liquid counterpart of LDA ice. There is only a remote possibility that transverse modes, which cannot propagate in the liquid state, can be responsible for the striking difference in thermal conductivity behavior of liquid water and LDA ice.[22] The two-liquid model suggests a glassy-liquid interrelation between LDA and liquid water unless a liquid-liquid phase line is crossed on cooling at 1 atm. If the hypothetical phase line between two liquids extends to negative pressures[23] then there is a thermodynamic basis for a first-order liquid-liquid transition on cooling, which cannot be observed due to crystallization. Quenching of liquid water to avoid crystallization would presumably also circumvent such a liquid-liquid transition. As a result, the produced state (ASW/HQW) would be a low-pressure (density) version of the glassy liquid that is formed by rapid cooling at high pressure, which is possibly high-density amorphous ice. In such a complex two-liquid scenario, the apparently different properties of LDA and ASW/HQW can be accounted for, but the crystalline like properties of LDA still remain to be explained.

As pointed out recently, the glass transition, which is the key characteristic for glassy liquids, cannot be regarded as established for the HDA and LDA states.[24] In numerous studies of the amorphous states there are either no anomalies at all near the expected glass transition temperature or these are weak and might be due to other reasons than a glass transition. This work focuses on the dielectric response of the high density amorphous ice, and is a more comprehensive and detailed study than one recently reported.[25] For a strongly polar substance, such as water, dielectric spectroscopy is a much more sensitive method than thermal methods for studies of molecular mobility. Thus, for cases where onset of molecular motions remains undetected due to a small heat capacity step at the glass transition, dielectric spectroscopy can easily reveal such motions and it is here used to establish the molecular reorientational relaxation behavior of the high density amorph. The amorph is produced by slow pressurization at 130 K and at this temperature the relaxation time is short enough to yield the fully relaxed high density amorphous state.[6,25] It will here be referred to as high density amorph or simply amorph, since the low-density amorph is not a subject in this study.

II. EXPERIMENT

The study was performed by using two different types of dielectric cells, a parallel plate capacitor of nominally 126–149 pF air capacitance and a concentric electrode capacitor of nominally 19 pF air capacitance. The change in geometry of the latter up to 1 GPa is insignificant when the pressure is hydrostatic.[26] The parallel plate capacitor consisted of six plates, each separated by the other by Polyetheretherketone (PEEK) spacers. The capacitor was placed inside a 37 mm internal diameter Teflon container which itself closely fitted inside the high-pressure cylinder of internal diameter 45 mm of a high-pressure assembly. The Teflon cell was filled with ~25 ml of pure water (tissue-culture grade water supplied by Sigma or water purified by using Milli-Q® Ultrapure Water Systems) or water doped with minute amount of KOH (1.7×10^{-4} mole fraction). The KOH-doping decreases the dielectric relaxation time in ice Ih due "to the release of water molecules from the ice rule"[27] so that the relaxation can be studied during the path towards amorphization. In the course of the experiments with the KOH dopant, the unexpected relaxation behavior of the amorph was established. As described below, the failure rate in these experiments is high and the demonstrated insignificant effect of doping on the relaxation behavior of the amorph justifies the use of also the data for the doped water to obtain a more complete picture.

The cell was sealed with a tightly fitting, 5 mm thick Teflon cover and the piston inserted. The whole assembly was placed in a vacuum chamber and load was applied by using a 5-MN hydraulic press. The pressure in the cell was determined from the ratio of load to area to which a correction for friction was applied. This correction had been previously established in a separate experiment by using the pressure dependence of the resistance of a manganin wire. The pressure of the hydraulic oil used to push the piston into the cylinder was computer controlled at the desired rate of increase or decrease. The temperature of the pressure vessel was varied by using a built-in helium cryostat equipped with heater. The capacitance and conductance of the dielectric capacitor immersed in the ice sample were measured, in real time, over the 0.8 Hz–1 MHz frequency range by means of a Solartron 1260 impedance analyzer. For pure water we used the same equipment for the concentrical capacitor and for the plate capacitor in the range 100 Hz–1 MHz. In the range 3 mHz–100 Hz, a HP33120A function generator was instead used to provide a sinusoidally varying signal over the sample capacitor and a reference capacitor placed in series. The voltages over the capacitors were measured simultaneously by two HP3457A voltmeters during at least one period (100 points), and the capacitance and conductance of the sample were determined for each frequency. The setup is the same as has been described previously,[28] but with new function generator and electronics.

The geometric capacitance of the capacitor was determined by using the known dielectric permittivity, ε', of ice Ih of 3.1±0.05 at 1 kHz to 10 kHz measurement frequency and ambient pressure and low temperatures, as reported by Johari *et al.*[29] (Johari and Whalley[30] had also found that for ice Ih, ε' at temperatures below 170 K at 10 kHz, was within 0.1% of the limiting high-frequency value of its dielectric permittivity, ε_∞, and Gough[31] has shown that ε_∞ decreases from 3.16 at 253 K to 3.093 at 2 K.) The results for the complex dielectric constant were calculated using the cell constant and ignoring the dimensional changes of the concentrical capacitor, which is valid under hydrostatic pressure conditions. In the case of the parallel plate capacitor, the distance between the plates will decrease on compression. Assuming isotropic compression of all the materials between the plates (also the PEEK spacers), then a ~30% volume decrease, as for the amorphization of ice Ih into the high density amorph at 130 K (1.08 cm^3 g^{-1} to 0.75 cm^3 g^{-1} [5]), yields ~10% decrease of the interplate distance. The permittivities of the amorph were corrected assuming isotropic compression. A comparison between the values for ε_∞ for two different amorphization experiments using the parallel plate capacitor and the single experiment using concentrical capacitor showed that the former gave 8% and 5% higher values, respectively. (In the experiment with the concentrical capacitor, the value for ε_∞ of ice Ih was recovered after the experiment showing that no permanent dimensional change had occurred during the experiment.)

The high-pressure vessel containing water at 0.05 GPa or lower pressure was cooled from room temperature to about 100 K at an average rate of ~15 K/h. After ice Ih had formed, the temperature was raised and stabilized at 125–130 K, which took a total of 10 h. This choice of temperature is a compromise between the decreasing pressure needed for amorphization at higher temperatures, which decreases the risk of failure of the pressure equipment (approximate limit ~1.5 GPa), and the increasing risk of crystallization at higher temperatures. Moreover, 130 K seems to be an appropriate temperature to obtain directly the fully relaxed high density amorphous ice. The pressure was then increased at the average rate of 0.1 GPa/h. The heating rate was typically 15 K/h and cooling rate, 10 K/h, near 150 K. Thus, one set of experiments took a continuous period of several days during which time the pressure and temperature of the sample were continuously monitored. The data are accurate to within ±0.05 GPa for pressure (at 1 GPa and 100 K), and ±0.3 K for temperature. The temperature difference between the sample and the Teflon cell wall was measured continuously during pressure and temperature cycling to determine water's transformation. Because of frequent rapid crystallization during pressurization through the amorphization range 0.8–1.1 GPa and breakage of the dielectric cell, the success rate in these experiments was only ~20%.

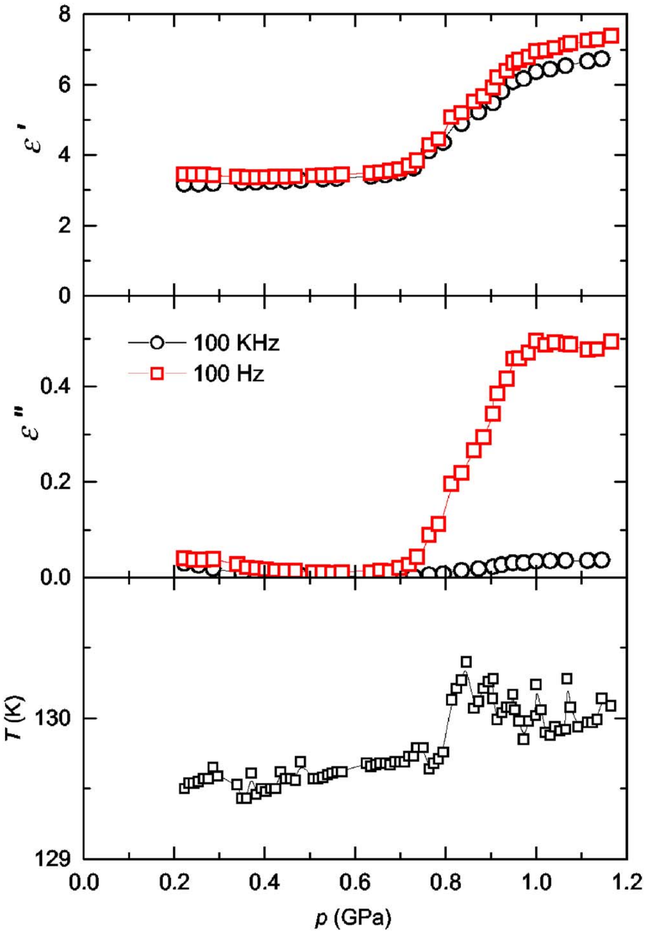

FIG. 1. (Color online) Dielectric permittivity ε', loss ε'', and sample temperature for pure ice as a function of pressure. Note that the dimensional changes of the capacitor have been ignored here.

III. RESULTS AND DISCUSSION

Figure 1 shows the dielectric permittivity ε' and loss ε'' for 100 Hz and 100 kHz frequencies on pressurization at ~130 K. The significant increase in the low frequency ε' and ε'' at about 0.7 GPa is due to the amorphization process and shows that an increasing number of H_2O molecules contributes to the dielectric relaxation process with increasing pressure. Simultaneously the high frequency ε' increases more significantly with pressure as the number of H_2O molecules per unit volume increases due to the abrupt densification. Despite slow pressurization rate of only 0.1 GPa h^{-1}, the temperature increases when the transformation rate increases at 0.8 GPa, which demonstrates the exothermic nature of the transition. The dielectric data show that the amorphization process is finished just above 1 GPa as the low frequency ε'' ceases to increase, and the increase in the high frequency ε' becomes less pronounced. The increase in the complex capacitance at the amorphization process varies somewhat between different runs, probably due to the deformation, and sometimes damaging, of the capacitor. This makes values for the static permittivity ε_0 and limiting high frequency permittivity ε_∞ somewhat uncertain (see experimental), but it does not affect the values for the dielectric relaxation times.

After amorphization, the temperature was lowered to ∼115 K and the pressure decreased to 0.41 and 1 GPa pressure, and the spectra recorded on slow heating. At 1 GPa, several pure samples as well as a sample doped with KOH were studied, and the results are shown in Figs. 2 and 3 (see also Fig. 2 in Ref. 25). The samples show similar dielectric behavior. A relaxation process appears and shifts to higher frequencies with increasing temperatures. On further heating the peak diminishes as the samples apparently crystallize. Simultaneously measured data for the temperature difference between the KOH-doped sample and the Teflon sample cell wall at 1 GPa shows a small exothermic peak at 148 K and just above a second more pronounced peak at 159 K (Fig. 4). One sample with pure water was cooled immediately after the first peak was observed. This changes the temperature gradients in the cell and the data have therefore been removed above the first peak. Despite cooling the sample, the crystallization did proceed. Thus, the doped and pure samples exhibit identical transition behavior. If we take into account the slower heating rate used here, then the temperature for the crystallization agrees with that commonly observed in other studies (∼165 K). The small initial exothermic peak at 1 GPa indicates onset of nucleation and the more significant can be due to slow crystal growth. The crystallization appears more abrupt at 0.41 GPa, and the resultant crystalline phase is also different at 0.41 than at 1 GPa. (The crystallization behavior depends on several parameters such as the heating rate and the microstructure of the sample. Since the latter can differ slightly between samples, e.g., due to the sluggishness of the amorphization process, the nature of the crystallization might vary between samples.) But the resulting states after crystallization cannot be determined here with certainty since the crystallization occurs in a metastable state, and the nature of the crystallization might therefore vary between different experiments. Klotz *et al.*,[32] found that slow heating of the D_2O amorph (∼0.5 K min^{-1}) at pressures near 1 GPa yielded crystallization into ices VI and XII, and heating near 0.4 GPa yielded crystallization into mainly ice IV. However, Salzmann *et al.*[4] found that the H_2O amorph crystallized into ices IV and XII at 1.15 GPa and ices V and IX at 0.5 GPa using a heating rate of ∼2 K min^{-1}. The resulting state after crystallization might thus depend on the experimental conditions such as sample size, D_2O or H_2O, and thermal history.

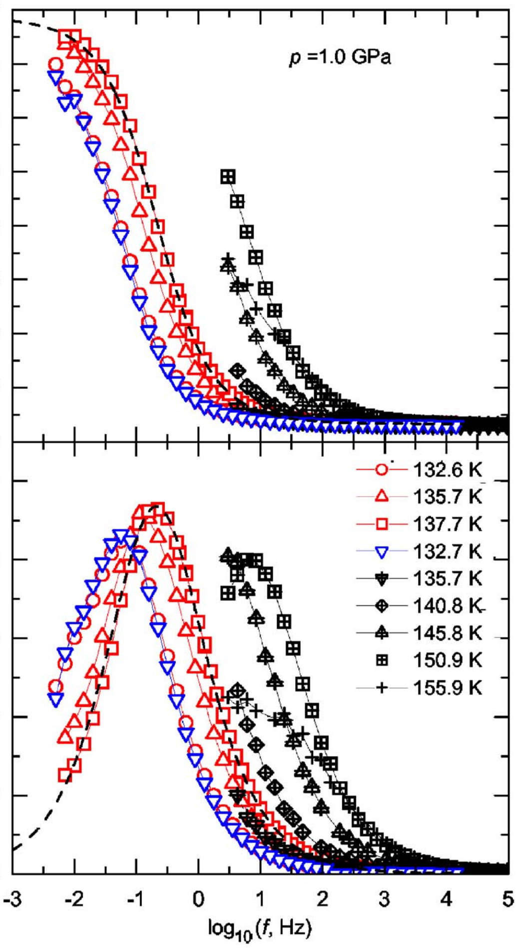

FIG. 2. (Color online) Dielectric spectra of the high density amorph (pure) on heating at 1 GPa. The data were obtained in two different experiments. The wide frequency range spectra (open red symbols) were obtained using a parallel plate capacitor and a special setup for low-frequency measurements. A subsequent cooling run, without exceeding 138 K, yielded the results at 132.7 K (blue symbols). The temperature was kept constant to within 0.1 K during all these measurements. The other spectra (black symbols filled with +) were obtained using a concentrical capacitor and measured on slow heating (0.3 K min^{-1}). The dashed line represents a fit of the Cole-Cole function given by Eq. (1).

One of the pure samples was studied in the temperature range 132–138 K, and then cooled without exceeding 138 K (Fig. 2). That is, it was cooled well below the temperature for the crystallization. A subsequent spectra obtained at 132.7 K, was identical to that obtained before heating to 138 K. This shows that the change in τ on heating is due mainly to the change in temperature. This suggests that the sample was fully relaxed and, thus, that a sample produced by slow pressurization to above 1.15 GPa at 130 K, and kept here of order of an hour due to the slow changes in the p,T conditions, yields the ultimate densified form recently referred to as very HDA (or vHDA). This is in accordance with the data for τ and the recent Raman data obtained on annealing of

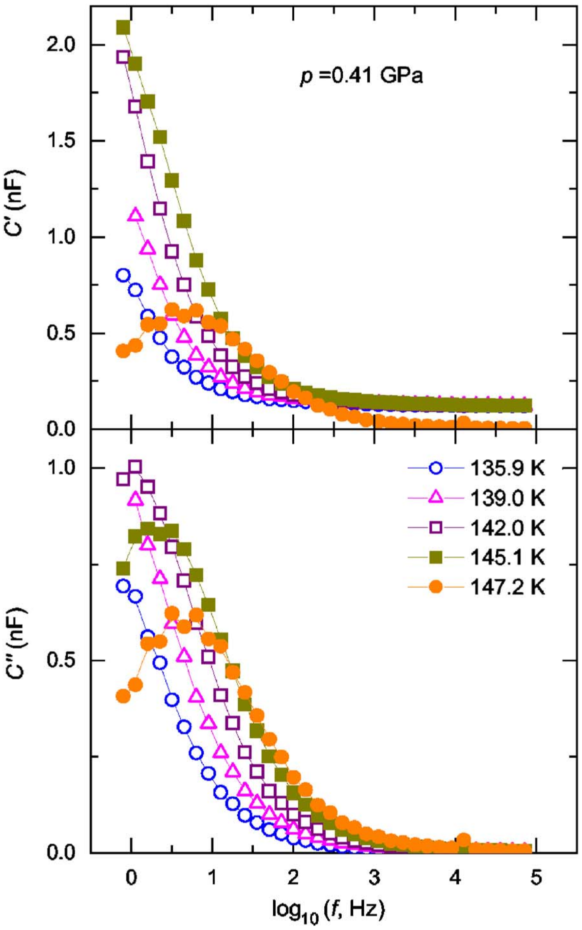

FIG. 3. (Color online) Dielectric spectra of the high density amorph (KOH-doped, 1.7×10^{-4} mole fraction) obtained on heating 0.3 K min^{-1} at 0.41 GPa. (The low values for C' and C'' are due to a damaged capacitor.)

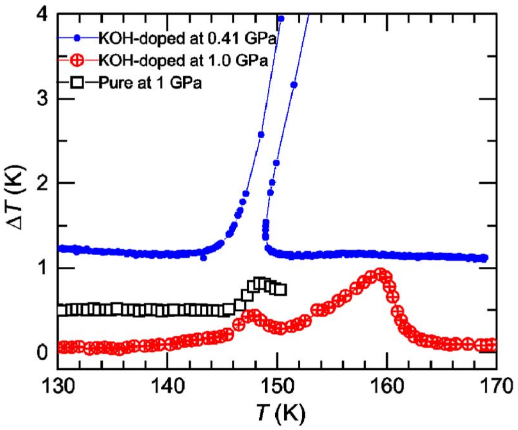

FIG. 4. (Color online) Temperature difference between the sample and the sample cell ΔT on heating of the high density amorph (pure and KOH-doped, 1.7×10^{-4} mole fraction). A baseline has been subtracted from the data, and the curves have been shifted vertically for clarity.

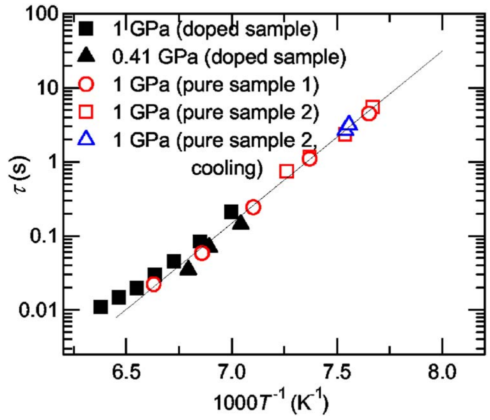

FIG. 5. (Color online) Dielectric relaxation times extracted from the peak of the loss spectra by direct reading or via superposition of the high frequency wing of the spectra onto the wide frequency range spectra measured in the temperature range 132–138 K. The line represents an Arrhenius fit to the data for the pure samples.

HDA at various temperatures near 1 GPa.[6] These data show that the gradual transformation to vHDA starts at temperatures where τ becomes of order of minutes and finishes at 130 K, where τ is of order of seconds, on isobaric heating near 1 GPa. The results in Fig. 2 also show that the relaxation strength changes reversible on heating. Since these are results obtained with the parallel plate capacitor, it is difficult to certify that it is an inherent feature of the high density amorph and not due to dimensional changes of the capacitor. Normally, a fully relaxed sample should expand on heating and the distance between the plates of the capacitor increase. If this is not accounted for then the relaxation strength should exhibit a slight apparent decrease. As shown here, the relaxation strength increases on heating up to 138 K and then decreases reversible on the subsequent cooling. Although this is opposite to the effect expected due to thermal expansion, further results are needed to ascertain this feature. The results for the doped sample at 1 GPa (Fig. 2 in Ref. 25) show similar behavior at temperatures below 149 K, i.e., below the temperature where significant crystallization can be observed. If this is a property of the amorph, then it indicates a temperature induced increase in the dipolar orientational correlation.

The relaxation times obtained from the peak values of the loss by direct reading, as well as by superposition of the spectra where the loss peak was outside the frequency range, are compiled in Fig. 5. The relaxation times for the doped sample agree well with those for the undoped. This shows that the dopant does not decrease τ as it does for hexagonal ice. In fact, it seems to slightly increase τ. The reason for the lack of significant effect of doping might be due to the amorphous structure, which makes the ice rules irrelevant, and/or segregation of the dopant during pressurization. It is believed that KOH doped ice I (cubic ice) exhibits a pressure induced phase separation because ionic impurities are known to segregate from the high pressure forms of ice.[33,34] If this occurs also on pressurization of ice Ih at 130 K, then the doped sample would (after amorphization) consist of a few small grains of KOH distributed randomly in the pure amorph, and this would explain the lack of difference between the doped and pure sample. A major or complete segregation of the dopant already on freezing liquid water during cooling at low pressure ($\sim$0.5 K min^{-1}) can be ruled out since τ for the doped ice Ih was shorter by several orders of magnitude compared to that for the pure sample.

The relaxation time is surprisingly short under these extreme conditions, which can be a consequence of relatively weak hydrogen bonding in comparison to those of HQW and crystalline ices,[16] and τ increases only slowly according to the Arrhenius behavior on cooling in the limited temperature range studied here. As mentioned above, the short τ is in correspondence with the recent results by Salzmann *et al.*[6] The calorimetrically observed glass transition temperature T_g corresponds commonly to a dielectric τ of order of 100 s. However, there are many exceptions showing both shorter and longer dielectric τ at T_g. As shown in Fig. 5, τ of the high density amorph becomes about 100 s at 122 K and 1 GPa, which is low in comparison with $T_g \sim 135$ K of ASW/HQW at atmospheric pressure.[35] [The T_g of ASW/HQW has been disputed[36,37] and a higher value of 165 K (Refs. 38 and 39) or 188 K (Ref. 40) has been suggested but the recent[41–43] and historical[20,44–46] direct experimental evidence for the low temperature value seems convincing.] Both reorientational and translational motions of H_2O molecules in liquid water with tetrahedral bonding require breaking and reforming of hydrogen bonds. As a consequence, the two processes are concomitant. This is proved by the validity of the Stokes-Einstein relations [47] down into the supercooled liquid temperature range at atmospheric pressure.[48,49] Moreover, it has been shown that the dielectric τ and the structural τ estimated from the T_g endotherm for amorphous solid water obtained by rapid cooling at atmospheric pressure are of the same order of magnitude at ambient pressure and 136 K.[50] The τ is estimated as $\sim$35 s at 136 K,[50] which agrees well with results for T_g obtained from a study of the molecular diffusion.[41] We therefore conclude that the arrest of reorientational motions observed at low temperature should be linked to the vitrification of the amorph, but that the dielectric τ is shorter than 100 s at T_g near atmospheric pressure, and it might be even shorter at high pressures. The very short dielectric τ at crystallization of only $\sim$30 ms suggest that the high density amorph transforms into an ultraviscous liquid well before crystallization commences.

As the logarithmic relaxation times vary linearly with the inverse temperature, these are described by Arrhenius behavior yielding an activation energy: $E_a = R\ (\partial \ln \tau / \partial T^{-1})_p$, where R is the gas constant, of 45 kJ mol^{-1} at 1 GPa. It appears to decrease somewhat at the highest temperature, but then the crystallization has commenced and this might have an effect on $\tau\,(T)$. The value for E_a can be compared with those of supercooled liquid water and ASW. The self-diffusion of supercooled water has been measured down to 238 K at atmospheric pressure, which yielded an activation energy of 44.4 kJ mol^{-1} at the lowest accessible temperature.[51] The activation energy appears to increase drastically on further temperature decrease and could even diverge at about 220 K, according to one of the models used to extrapolate the data to lower temperatures.[51] The apparent activation energy for self-diffusion in thin ASW films at atmospheric pressure in the range 140–150 K is reported as 170 ± 40 kJ mol^{-1},[43] and the data extrapolate reasonably well to those of supercooled water using a Vogel-Fulcher-Tammann equation.[52–54] (A much smaller value for E_a of 14 kJ mol^{-1}, in the range 100–140 K, is reported for diffusion vertically through the first bilayers of amorphous films.[55]) The activation energy for HQW in the range 135–150 K is estimated as 55 ± 5 kJ mol^{-1}.[45] Although this value obtained from differential scanning analysis should be treated with caution, it agrees roughly with that obtained in a dielectric study of water sequestered in the pores of a polymer in the 160–190 K range, which yielded $E_a = 61$ kJ mol^{-1}.[56]

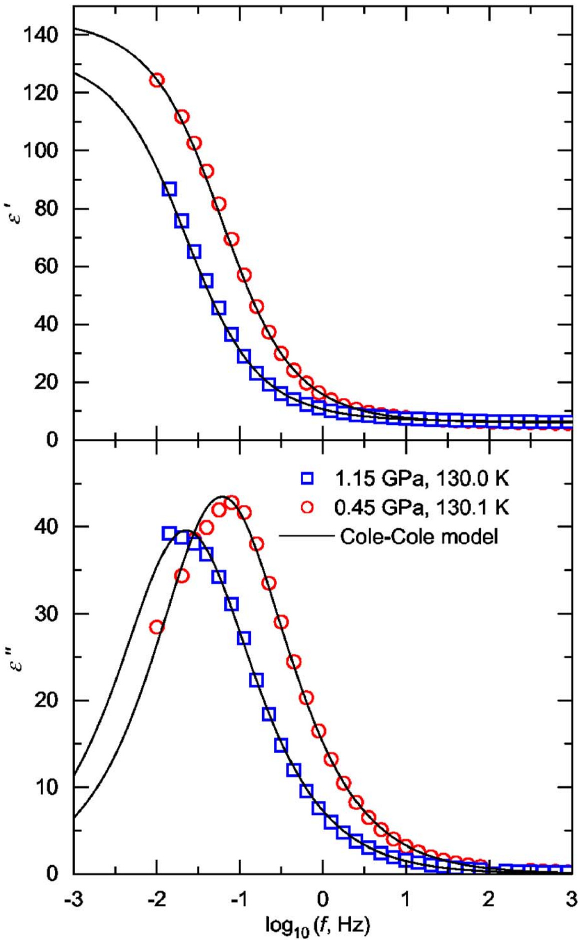

FIG. 6. (Color online) Dielectric spectra of the high density amorph (pure) on depressurization at 130 K. The lines represent the fitted Cole-Cole model given by Eq. (1).

It has been shown that E_a of liquid water decreases with pressure at room temperature. This has been investigated up to 0.4 GPa by Wilbur *et al.*[57] in their diffusion studies of heavy water. They found that E_a decreased most strongly at the initial pressurization near atmospheric pressure, and at 0.4 GPa it had decreased to 70% of its ambient pressure value. The value obtained here for E_a of the high density amorph at 1 GPa is about 25% of that for self-diffusion of ASW at 140 K, about the same as that for liquid water at 240 K and ambient pressure, and 80% of that for structural relaxation of HQW. Consequently, it is too small compared to that obtained for self-diffusion of ASW using $(\partial E_a / \partial p)_T$ of liquid water at room temperature for extrapolation, but might be reconciled with values for the structural relaxation of

HQW and dielectric relaxation of sequestered water at atmospheric pressure.

Results for the pressure induced change of the spectra are shown in Fig. 6. The relaxation time changes weakly with pressure in comparison with temperature. The extracted values for τ yield $(\partial \ln \tau/\partial p)_T = 1.5\ \mathrm{GPa}^{-1}$ in the pressure range 0.45 to 1.15 GPa. This means that a pressure increase of 1 GPa, would shift T_g of the process to 5 K higher temperatures, which can be deduced together with the data in Fig. 5. (From the isobaric results for τ in Fig. 4 of Ref. 25 we deduce a corresponding value of 3–5 K GPa^{-1} in the range 142–148 K.) From the pressure dependence of τ, it follows that the relaxation process has an apparent activation volume: $\Delta V^* = RT\ (\partial \ln \tau/\partial p)_T$, of 1.7 cm^3 mol^{-1} at 130 K. (An estimate at 145 K, using the data at 0.41 GPa and 1 GPa for the doped sample yields $\Delta V^* = 0.5$ cm^3 mol^{-1}.) The activation volume is the volume change needed for the relaxation process in addition to the available free volume. The $\Delta V^* = 1.7$ cm^3 mol^{-1} corresponds to 2.8 Å^3 per molecule, i.e., it is 13% of the average volume available to each molecule ($\sim$22 Å^3).

The glass transition temperature of a substance varies with pressure typically in the same manner as the viscosity of the liquid state. The viscosity of water at 273 K decreases on compression up to 0.15 GPa and then increases and reaches the same value at 0.3 GPa as that at 0.1 MPa.[58,59] This unusual feature of a pressure induced decrease of the viscosity is most pronounced and continues up to higher pressures at the lowest temperature, in the investigated range of 258–283 K. This suggests that the tendency would persist at low temperatures and could be even more pronounced. If this is indeed the case, then it follows that the glass transition temperature would be almost independent of pressure. In fact, it could even decrease initially with increasing pressure, which would be yet another unique feature of water. Thus, the weak pressure dependence for τ observed here, and the correspondingly small ΔV^*, are in qualitative agreement with viscosity results for water at 273 K.

If the pressure dependence of T_g: $dT_g/dp = 5$ K GPa^{-1} for the amorph formed at 1 GPa persists down to atmospheric pressure, then the dielectric results would formally indicate a calorimetric T_g of 117 K, but it is most likely higher as it probably corresponds to shorter dielectric τ than 100 s. The pressure dependence could also be weaker or even negative near atmospheric pressure, which is indicated by the behavior of liquid water near room temperature. In any case, 117 K is close to that for the transition to LDA.[5] Since the transformation into LDA ice intervenes, it is probably not possible to observe T_g at atmospheric pressure.

The results in Fig. 6 show that the relaxation strength decreases with increasing pressure and resembles the behavior observed on cooling, shown in Fig. 2. Consequently, the data provide evidence for a process that gradually decreases ε_0 of the high density amorph on cooling as well as on pressurization.

The dielectric spectra are best described by the symmetrical τ distribution function given by Cole and Cole[60]

$$\varepsilon^*(\omega) = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)/[1 + (i\omega\tau_{\mathrm{cc}})^{1-\alpha}], \qquad (1)$$

where $\omega(=2\pi f)$ is the angular frequency, τ_{cc} is the Cole-Cole relaxation time, and 1-α is a distribution factor with a value in the range 0 to 1. This type of distribution has been found also for water in the range 273–323 K.[61] Both the results for doped and pure samples at all pressures could be well described by the function. The fitted value for ε_0 of the pure high density amorph is $\varepsilon_0 = 157$ at 137.7 K and 1 GPa. (The value has an uncertainty of $\sim$8% since the dimensional changes of the capacitor can only be roughly accounted for; see experimental.) The distribution factor is $1-\alpha = 0.70$, and it is almost independent of pressure.

It is difficult to estimate accurately the value for ε_0 of supercooled water at 1 GPa and 140 K, which is produced by a reversible path, and not as is it seems here through an irreversible path. In theory, such state could be obtained by first pressurization of liquid water above room temperature up to 1 GPa, and then cooling to 140 K. Alternatively, liquid water could be cooled at atmospheric pressure and pressurized isothermally at low temperatures. In practice, it would not be possible to avoid crystallization during these two different paths into either ice VI or ice I, respectively. However, we may try to estimate the changes in ε_0 during either of the paths from the known values. The value at 273 K and atmospheric pressure ($\varepsilon_0 = 88$) (Ref. 62) increases by slightly more than 20% at 1 GPa, by extrapolation of lower pressure data.[62,63] Ice I has somewhat larger value for ε_0 than water at atmospheric pressure ($\varepsilon_0 = 92$ at 273 K) (Ref. 62) and it increases in a similar manner as that for supercooled water upon cooling. The value for ε_0 of ice Ih is about 185 at 140 K.[30] If liquid water follows the behavior of ice Ih on cooling and the pressure dependence for ε_0 of liquid water at 273 K would persist at low temperatures then this yields $\varepsilon_0 \sim 220$ at 1 GPa and 140 K, i.e., it is significantly larger than the measured values. The same apparent discrepancy arises in a comparison of the density. At 1 GPa, the density for liquid water near room temperature is about $\sim$1.25 g cm^{-3} (Ref. 63) and that of the amorph is $\sim$1.33 g cm^{-3} at 130 K, which shows that the average thermal expansion coefficient must be as large as 3.6×10^{-4} K^{-1} on cooling at 1 GPa. This is much different from that of supercooled water at ambient pressure, which has a negative thermal expansion coefficient. Although the thermal expansion coefficient becomes positive at high pressures, there seems to be a discrepancy between the density of the amorph and that estimated for supercooled liquid water at high pressure.

In statistical theories, ε_0 is given by the Kirkwood-Fröhlich equation[64–66] as (in SI-units)

$$\frac{(2\varepsilon_0 + \varepsilon_\infty)(\varepsilon_0 - \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2} = \frac{N_A \rho}{9 M k_B T \varepsilon_{vac}} \mu_g^2 g_K, \qquad (2)$$

where N_A is Avogadro's number, ρ is the density, M is the molar mass, k_B is the Boltzmann constant, T is the temperature, μ_g is the dipole moment of an isolated molecule in the vapor phase, and ε_{vac} is the permittivity of vacuum (8.85×10^{-12} F m^{-1}). The quantity g_K is the orientational or dipolar correlation factor introduced by Kirkwood. It is a measure of the local ordering and the correlation of the near-neighbor dipoles, given by $g_K = 1 + \Sigma_i z_i \cos \gamma_i$, where z_i is the number of correlating dipoles and γ_i is the angle between them. When g_K is greater or less than unity it indicates a predominantly parallel or antiparallel alignment of dipole vectors, respectively. Thus g_K is a useful source of information about intermolecular interactions.

The appropriate value for ε_∞ in Eq. (2) has been debated.[67] In his original paper, Kirkwood[64] used the value for the refractive index n to obtain ε_∞, i.e., $\varepsilon_\infty = n^2$, and we also use this relation, which is the most common and classical approach used for water and the ice phases. But since water and ice have absorption in the far infrared bands, it may perhaps be more appropriate to use the limiting high frequency dielectric permittivity than n^2 based on visible light. A value for g_K of liquid water, $g_K = 1.9$, derived from neutron scattering data falls in between these two approaches.[68] (The high frequency ε' approaches 4–5[49,67] and $\varepsilon_\infty = 4.5$ yields $g_K \sim 1$, whereas the optic $n^2 = 1.33^2$ yields $g_K \sim 2.9$.) We therefore provide also the value using the limiting high frequency dielectric constant in parentheses. The absolute values of g_K for water are thus somewhat uncertain but express the change of the dipolar orientational correlation between the phases.

Assuming constancy of the Lorenz-Lorenz function, i.e., $(n^2-1)/(n^2+2) = \rho \times$ const, we estimate $n^2 = 1.45^2$ for the amorph at 1 GPa [$\rho = 1.33$ g cm^{-3} at 1 GPa (Ref. 6)] using data for liquid water at atmospheric pressure. Together with $\mu_g = 1.855$ D (Ref. 69) and the value for $\varepsilon_0 = 157$ at 138 K obtained here, this yields $g_K = 1.7$. [$\varepsilon_\infty = 5$ (Ref. 70) yields $g_K = 0.6$.]

The value for g_K of liquid water at atmospheric pressure and 273 K is ~ 2.9 using the values given above, and it decreases slightly with increasing temperature. It also decreases with increasing pressure, which has been studied up to 0.3 GPa ($\sim 10\%$ GPa^{-1}).[71] For ice Ih, the value is ~ 3.4 (1.8) at atmospheric pressure and it is almost independent of temperature. For ice VI, the stable phase under these conditions, ε_0 is as high as 325 at 150 K,[72] and g_K is 3.4 (1.2) at 243 K.[73] Consequently, the dipolar orientational correlation is significantly less strong in the amorph than in ice VI at 1 GPa, and ice Ih and liquid water at atmospheric pressure. [As indicated by the results for $\varepsilon_0(T)$, g_K of the amorph may increase with increasing temperature, which is opposite of the normal behavior.]

A change to a less polar water structure has been discussed by Grünwald[74] in terms of a two-state model, where one is the common four-coordinated state and the other is a five-coordinated state. He concluded that a five-coordinated water structure can be significantly less polar than a four-coordinated one, and a change into the former seems to be consistent with the experimentally observed increase in the nearest neighbor coordination number from a bit more than four in atmospheric pressure liquid water to five in the high density amorph under atmospheric pressure conditions. The five-site structure was realized by two complimentary five-coordinated structures, one with two donor and three proton acceptor sites and the other with two acceptor and three donor sites, fulfilling the requirement of two donors and two acceptor sites in average. Although the structure of the high density amorph has been described as a tetrahedrally coordinated fully hydrogen bonded structure, it might be worth to consider the possibility of "inertial" molecules taking part in the near-neighboring hydrogen bonded network, as in the model of Grünwald,[74] which could imply constraints on the effective dipolar moment. Moreover, the model implies weakened hydrogen bonding in agreement with experimental findings.[16] A tetrahedrally coordinated network can also, of course, be arranged so that the effective dipolar moment is small, which is realized in *crystalline* antiferroelectric phases such as ices II and IX. In any case, it is obvious that the structure of the amorph must fulfill the constraints of a static dielectric permittivity which is unusually low under these low temperature high pressure conditions.

IV. CONCLUDING REMARKS

The dielectric results for the high density amorphous state of ice show that the amorph relaxes within seconds at 130 K at 1 GPa. These results agree well with the recent findings, which show that the volume of the amorph relaxes slowly at 120 K and is fully relaxed after heating to above 130 K near 1 GPa.[6] The short relaxation time is surprising and indicates that the amorph is in a metastable equilibrium state at temperatures above 130 K, i.e., an ultraviscous liquid state, well before it crystallizes on further heating. The static dielectric permittivity of the amorph is relatively low, yielding a significantly lesser dipolar orientational correlation than that of the crystalline phases Ih and VI, and liquid water under normal conditions. This result puts constraints on the amorphous structure and appears to advocate a five-coordinated network structure, as described in the model of Grünwald.[74]

The finding of the short τ of 30 ms at 150 K, i.e., near crystallization, and which is only weakly dependent of pressure, provides a new picture of the dynamics of the high density amorph and is a help in the challenge for relating it to liquid water at ambient pressure. The state of ultraviscous water at 1 GPa is the state that could be obtained by a route whereby water is pressurized above room temperature and cooled at 1 GPa rapidly enough to avoid crystallization to ice VI. However, before the state of the high density amorph, just prior to crystallization, can be confidently linked to high-pressurized liquid water, its seemingly different properties from high-pressurized liquid water such as density, static permittivity and, possibly, activation energy must be accounted for.

ACKNOWLEDGMENTS

H. Suga and G. P. Johari are gratefully acknowledged for helpful discussions. This is contribution No. 102 from the Research Center for Molecular Thermodynamics, Osaka University.

*Electronic address: ove.andersson@physics.umu.se
†Electronic address: inaba@chem.sci.osaka-u.ac.jp

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

[2] O. Mishima, L. D. Calvert, and E. Whalley, Nature (London) **314**, 76 (1985).

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

[4] C. G. Salzmann, E. Mayer, and A. Hallbrucker, Phys. Chem. Chem. Phys. **6**, 5156 (2004).

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

[6] C. G. Salzmann, T. Loerting, S. Klotz, P. W. Mirwald, A. Hallbrucker, and E. Mayer, Phys. Chem. Chem. Phys. **8**, 386 (2006).

[7] M. M. Koza, T. Hansen, R. P. May, and H. Schober, cond-mat/0602207 (unpublished).

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

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

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

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

[12] S. Klotz, Th. Strässle, R. J. Nelmes, J. S. Loveday, G. Hamel, G. Rousse, B. Canny, J. C. Chervin, and A. M. Saitta, Phys. Rev. Lett. **94**, 025506 (2005).

[13] R. Martonak, D. Donadio, and M. Parrinello, J. Chem. Phys. **122**, 134501 (2005).

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

[15] H. Schober, M. M. Koza, A. Tölle, C. Masciovecchio, F. Sette, and F. Fujara, Phys. Rev. Lett. **85**, 4100 (2000).

[16] D. D. Klug, C. A. Tulk, E. C. Svensson, and C.-K. Loong, Phys. Rev. Lett. **83**, 2584 (1999).

[17] A. I. Kolesnikov, J. Li, S. F. Parker, R. S. Eccleston, and C.-K. Loong, Phys. Rev. B **59**, 3569 (1999).

[18] O. Andersson and A. Inaba, Phys. Chem. Chem. Phys. **7**, 1441 (2005).

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

[20] A. Hallbrucker, E. Mayer, and G. P. Johari, J. Chem. Phys. **93**, 4986 (1989).

[21] P. G. Debenedetti, J. Phys.: Condens. Matter **15**, R1669 (2003).

[22] O. Andersson and H. Suga, Netsu Sokutei **32**, 232 (2005).

[23] H. Tanaka, Nature (London) **380**, 328 (1996).

[24] M. M Koza, B. Geil, H. Schober, and F. Natali, Phys. Chem. Chem. Phys. **7**, 1423 (2005).

[25] O. Andersson, Phys. Rev. Lett. **95**, 205503 (2005).

[26] G. P. Johari, A. Laverne, and E. Whalley, J. Chem. Phys. **61**, 4292 (1974).

[27] S. Kawada, J. Phys. Soc. Jpn. **57**, 3694 (1988).

[28] H. Forsman, J. Phys. D **22**, 1528 (1989).

[29] G. P. Johari, Contemp. Phys. **22**, 613 (1981); G. P. Johari and S. J. Jones, Philos. Mag. B **54**, 311 (1986).

[30] G. P. Johari and E. Whalley, J. Chem. Phys. **75**, 1333 (1981).

[31] S. R. Gough, Can. J. Chem. **50**, 3046 (1972).

[32] S. Klotz, G. Hamel, J. S. Loveday, R. J. Nelmes, and M. Guthrie, Z. Kristallogr. **218**, 117 (2003).

[33] S. R. Gough and D. W. Davidson, J. Chem. Phys. **52**, 5442 (1970).

[34] H. Suga, T. Matsuo, and Y. Yamamuro, Pure Appl. Chem. **64**, 17 (1992).

[35] G. P. Johari, J. Chem. Phys. **119**, 2935 (2003).

[36] I. Kohl, L. Bachmann, E. Mayer, A. Hallbrucker, and T. Loerting, Nature (London) **435**, E1 (2005).

[37] Y. Yue and C. A. Angell, Nature (London) **435**, E1 (2005).

[38] V. Velikov, S. Borick, and C. A. Angell, Science **294**, 2335 (2001).

[39] S. Cerveny, G. A. Schwartz, R. Bergman, and J. Swenson, Phys. Rev. Lett. **93**, 245702 (2004).

[40] N. Giovambattista, C. A. Angell, F. Sciortino, and H. E. Stanley, Phys. Rev. Lett. **93**, 047801 (2004).

[41] R. Souda, J. Chem. Phys. **122**, 134711 (2005).

[42] A. Minoguchi, R. Richert, and C. A. Angell, Phys. Rev. Lett. **93**, 215703 (2004).

[43] R. S. Smith, Z. Dohnálek, G. A. Kimmel, K. P. Stevenson, and B. D. Kay, Chem. Phys. **258**, 291 (2000).

[44] J. A. McMillan and S. C. Los, Nature (London) **206**, 806 (1965).

[45] M. Sugisaki, H. Suga, and S. Seki, Bull. Chem. Soc. Jpn. **41**, 2591 (1968).

[46] G. P. Johari, A. Hallbrucker, and E. Mayer, Nature (London) **330**, 552 (1987).

[47] H. J. V. Tyrrell and K. R. Harris, *Diffusion in Liquids* (Butterworth, London, 1984).

[48] H. R. Pruppacher, J. Chem. Phys. **56**, 101 (1972).

[49] C. Rønne, L. Thrane, P.-O. Åstrand, A. Wallqvist, K. V. Mikkelsen, and S. R. Keiding, J. Chem. Phys. **107**, 5319 (1997).

[50] G. P. Johari, Phys. Chem. Chem. Phys. **7**, 1091 (2005).

[51] W. S. Price, H. Ide, and Y. Arata, J. Phys. Chem. A **103**, 448 (1999).

[52] H. Vogel, Phys. Z. **22**, 645 (1921).

[53] G. S. Fulcher, J. Am. Ceram. Soc. **8**, 339 (1925).

[54] G. Tammann and W. Hesse, Z. Anorg. Allg. Chem. **156**, 245 (1926).

[55] K.-H. Jung, S.-C. Park, J. -H Kim, and H. Kang, J. Chem. Phys. **121**, 2758 (2004).

[56] K. Pathmanathan and G. P. Johari, J. Polym. Sci., Part B: Polym. Phys. **28**, 675 (1990).

[57] D. J. Wilbur, T. DeFries, and J. Jonas, J. Chem. Phys. **65**, 1783 (1976).

[58] F. T. Worrell, Nature (London) **207**, 620 (1965).

[59] T. DeFries and J. Jonas, J. Chem. Phys. **66**, 896 (1977).

[60] K. S. Cole and R. H. Cole, J. Chem. Phys. **9**, 341 (1941).

[61] K. Okada, M. Yao, Y. Hiejima, H. Kohno, and Y. Kajihara, J. Chem. Phys. **110**, 3026 (1999).

[62] *CRC Handbook of Chemistry and Physics*, edited by D. R. Lide, 86th ed. (CRC Press, Boca Raton, FL, 2005–2006).

[63] W. B. Floriano and M. A. C. Nascimento, Braz. J. Phys. **34**, 38 (2004).

[64] J. G. Kirkwood, J. Chem. Phys. **7**, 911 (1939).

[65] H. Fröhlich, *Theory of Dielectrics* (Clarendon Press, Oxford, 1949).

[66] C. J. F. Böttcher, *Theory of Electric Polarization*, 2nd ed. (Elsevier, Amsterdam, 1973), Vol. 1.

[67] N. E. Hill, W. E. Vaughan, A. H. Price, and M. Davies, *Dielectric Properties and Molecular Behaviour* (Van Nostrand Reinhold Company, London, 1969).

[68] A. K. Soper, J. Chem. Phys. **101**, 6888 (1994).

[69] F. J. Lovas, J. Phys. Chem. Ref. Data **7**, 1445 (1978).

[70] The measured values for the high frequency permittivity at 100 kHz probe frequency vary relatively strongly with temperature. The measured value at 130 K and 1 GPa is 5.65 for the

concentrical capacitor, and it decreases to 5.3 at 115 K. Thus, a reasonable estimate for the amorph is $\varepsilon_\infty=5$, which is close, to that for the stable phase ice VI, which is $\varepsilon_\infty=5.1$, as reported by M. Wilson *et al.*, J. Chem. Phys. **43**, 2384 (1965) (Ref. 73).

[71] K. R. Srinivasan and R. L. Kay, J. Chem. Phys. **60**, 3645 (1974).

[72] G. P. Johari and E. Whalley, J. Chem. Phys. **64**, 4484 (1976).

[73] G. J. Wilson, R. K. Chan, and D. W. Davidson, J. Chem. Phys. **43**, 2384 (1965).

[74] E. Grünwald, J. Am. Chem. Soc. **108**, 5719 (1986).