Dielectric Relaxation of Low-Density Amorphous Ice under Pressure

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In situ studies at high pressures show that the dielectric relaxation time τ of low-density amorphous (LDA) ice is more than an order of magnitude longer than that of high density amorphous ice. The increase in τ at the transformation to LDA ice with a simultaneous large density decrease shows that, despite an increase in the average intermolecular distance, the structural change leads to restriction for the orientational diffusion of H_2O. The origin is most likely the same as in ice I, i.e., due to the ice rules. This result further stresses the crystallinelike nature of LDA ice.

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The two amorphous solid states of water, high and low-density amorphous ices, which are produced through pressure induced amorphization at low temperatures [1] provide an experimental foundation for the two-liquid model of water, i.e., that water at low temperatures may exist simultaneously in two distinct liquid phases of different densities. These could be liquid counterparts of the two amorphous ices and formed via glass transitions upon heating, but experimental proofs for two liquids are scarce. The two-liquid model has been used to interpret several unusual low-temperature behaviors of water such as the density maximum and increase of heat capacity and compressibility upon cooling. The apparent divergence of compressibility and extrapolation of its value to infinity at low temperatures, where experimental investigations seem impossible due to rapid crystallization, has been suggested as being due to a second critical point of water. It has been conjectured that the two-liquid water phases can exist in equilibrium and that the equilibrium phase line ends at the second critical point. This scenario is supported by computer simulations [2], and data for emulsified water also indicate the existence of a phase line that terminates in a manner expected for a critical point [3].

High density amorphous ice (HDA) is formed if ice I*h* or ice I*c* is pressurized to above ~1.5 GPa at 77 K. Upon heating at a rate ~3 K min^{-1} from 77 K near or at ambient pressures it transforms further to low-density amorphous ice (LDA) at ~117 K [4]. However, if the high density amorph is produced by isothermal pressurization at higher temperatures, or annealed at high temperatures and pressures, typically in the range 120–150 K at 1 GPa, after production at 77 K, it becomes more dense and stable [5,6]. This is reflected in an increase of the HDA to LDA transition temperature [4]. Moreover, neutron and x-ray scattering studies have shown that HDA converts to LDA isothermally at different temperatures, beginning at ~95 K [7]. Alternatively, LDA can be produced at ~130 K by isothermal depressurization of HDA to low pressures [8,9].

The two-liquid model with a second critical point at ~220 K and ~0.1 GPa [3] suggests that LDA is the glassy counterpart of liquid water near atmospheric pressure. But apart from the amorphous x-ray pattern, LDA shows many similarities with ice I*h* and ice I*c* and distinct differences from amorphous solid water formed by hyperquenching liquid water or condensing water vapor onto a cold plate. Based on molecular dynamics calculations and the properties of LDA, it has recently been proposed that LDA may be simply an incompletely recovered ice I*h* [10]. LDA exhibits crystallinelike thermal conductivity [9], and inelastic incoherent neutron scattering spectra show strong similarities between LDA and ices I*h* and I*c* [11,12]. Moreover, results for inelastic x-ray scattering show phonon propagation up to unusually high frequencies [13].

The suggestion of a third distinct amorphous state, very high density amorphous (VHDA) ice , which is produced by heating of HDA to 130 K at ~1 GPa [5,6], also provides a complication to the understanding of the amorphous solid water states and, accordingly, to the two-liquid model. The gradual densification of HDA observed on heating near 1 GPa [5] is indicative of a relaxation process, and an alternative description of the state formed on heating is a relaxed (more dense) HDA referred to as rHDA [6]. In this Letter, we use rHDA to denote the state produced by heating HDA near 1 GPa, or by amorphization of ice I*h* near 130 K.

The structures of the amorphous states produced under pressure have been studied in several recent investigations [7,14–17]. All the amorphous states exhibit tetrahedrally coordinated fully hydrogen bonded networks. Moreover, (r)HDA has extra, nonhydrogen bonded, molecules in interstitial positions whereas LDA exhibits no such interstitial molecules [15,16]. The structure of LDA shows local-order similarities with ices I*h* and I*c*, with a nearest neighbor coordination which is close to 4.

Further positive or negative proofs for the liquid states of the solid amorphous ices are very important for progressing the understanding of water's low-temperature properties. We have recently obtained positive evidence for that rHDA transforms into a liquid state well before it crystallizes on heating using dielectric spectroscopy, *in situ*, at high pressures [18,19]. Here we report the corresponding

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data for LDA. As dielectric spectroscopy probes dipole motions, it provides a very sensitive probe for the mobility of the highly polar water molecule. However, despite a 25% density decrease at the rHDA to LDA transition, we show here that the latter exhibits significantly longer dielectric relaxation time τ before it crystallizes into ice I*c* with simultaneous further increase of τ.

The study was performed by using a parallel plate capacitor of nominally 149 pF air capacitance, which consisted of six plates, each separated by the other by polyetheretherketone (PEEK) spacers. The capacitor was placed inside a Teflon container, filled with ca. 25 ml of pure water, which itself closely fitted inside the high-pressure cylinder. The whole assembly was placed in a vacuum chamber and load was applied via a steel piston. The temperature was varied by using a built-in helium cryostat equipped with heater, and measured both in the sample and the Teflon cell. The data are accurate to within ±0.05 GPa for pressure (at 1 GPa and 100 K) and ±0.3 K for temperature. The complex capacitance was measured using a Solartron 1260 impedance analyzer above 100 Hz, whereas a HP33120A function generator was used below 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, and the capacitance and conductance of the sample were determined for each frequency. The geometric capacitance of the capacitor was determined by using the known high-frequency dielectric permittivity of ice I*h* of 3.1 at low pressures, and the change with pressure was roughly taken into account [19].

After rHDA had been obtained by pressurization (~0.1 GPa/h) to above 1.15 GPa at ~130 K, the two different routes to obtain LDA were studied in several runs. Results on heating at low pressures are shown in Fig. 1 together with previously measured data for thermal conductivity [20]. The dielectric permittivity ε' and loss ε'' at constant frequency of 0.3 Hz show the expected transitions sequence: rHDA → LDA and LDA → ice I*c* on heating. The ε'' of rHDA increases on heating, but decreases abruptly at the rHDA to LDA transition onset at about 125 K. The simultaneously measured temperature data shows a peak, indicating the maximum transition rate, at 135 K. LDA is metastable in a limited temperature range and then transforms further to ice I*c* at a temperature which is in good agreement with previous data.

Since the time to obtain a low-frequency spectrum is significant and the transition from rHDA to LDA evolves with time, it is not possible to study the permittivity in a wide frequency range even on slow heating. Results for spectra above ~0.3 Hz are shown in Fig. 2, which corresponds to a temperature shift of about 0.5 K during each spectrum. Only the high-frequency wing of the loss peak in rHDA can be observed at these frequencies [18,19]. The spectra show that it moves towards higher frequencies with increasing temperatures, but before the loss peak can be observed, the transition to LDA intervenes and the loss

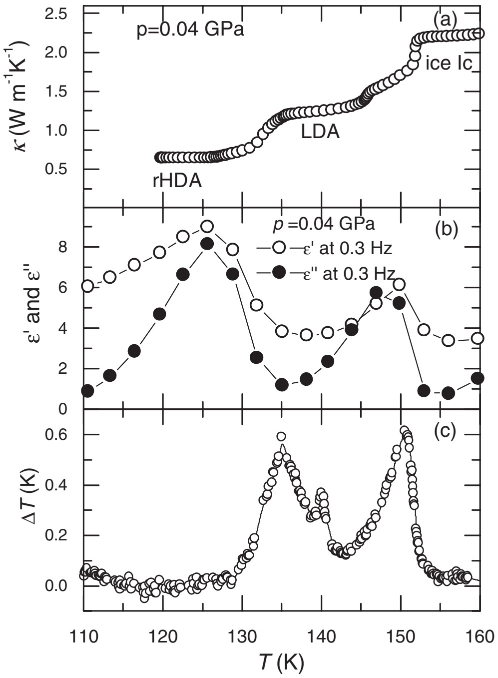

FIG. 1. (a) The thermal conductivity κ [20], (b) dielectric permittivity ε' and loss ε'' at 0.3 Hz probe frequency, and (c) sample excess temperature ΔT as a function of temperature at 0.04 GPa.

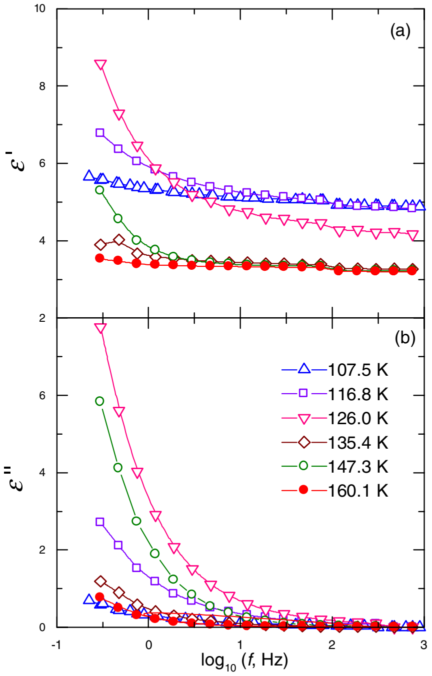

FIG. 2 (color online). The dielectric permittivity ε' and loss ε'' as a function of frequency on heating (~0.3 K/min) at about 0.03 GPa. The loss peak moves to higher frequencies with temperature, but shifts to lower frequencies at the rHDA to LDA (~130 K) and LDA to I*c* (152 K) transitions due to increasing τ.

decreases significantly. Simultaneously, the high-frequency data for ε' show a significant decrease at the transition to LDA due to the density decrease. A decrease in the low-frequency ε'' can be observed also at the LDA to ice I*c* transition, but there is no change in the high-frequency ε', which is due to the insignificant density change.

The second route to obtain LDA through depressurization at temperatures near 130 K yielded the same results in two runs, and those for one are depicted in Figs. 3 and 4. The data for ε' and ε'' at 0.1 Hz (Fig. 3) show clearly a two step transition sequence at 0.45 and 0.85 GPa on the subsequent pressurization. The spectra are unaffected up to ~0.35 GPa, where a loss peak with the same τ as that of rHDA grows with increasing time and pressure. At 1.1 GPa, the relaxation peak associated with rHDA is fully recovered via significant grows at 0.45 and 0.85 GPa. This result is in very good agreement with the transition sequence "LDA → HDA" at 0.45 GPa and "HDA → VHDA" at 0.95 GPa on isothermal pressurization of LDA at 125 K [21]. Consequently, the transition sequence seems to be identical and, thus, that 100% LDA was produced on depressurization. But because the experimental procedure used here does not allow the recovery of the sample at 77 K for a structural analysis, as done by Loerting *et al.* [21], one cannot be certain concerning the state of the sample. A previous study has shown that also ice I (presumable I*c*) can be formed during isothermal depressurization [22]. (LDA produced through heating of (r)HDA at low pressures [21], invariably yields LDA before ice I on further heating.) This possibility cannot be ruled out and the transition sequence could thus be LDA → rHDA and ice I → rHDA, i.e., the initial state would be a mixture of LDA and ice I. The potential mixture then contains slightly more than 50% LDA, which can be deduced from the relaxation strength or the high frequency ε' in the range 0.5–0.6 GPa. It follows that the sample at pressures below 0.4 GPa consists of 50–100% LDA. Moreover, the good agreement between τ at 0.55 GPa and that of (bulk) rHDA certifies that the rHDA domain size, and therefore also the LDA domain size, must be large and therefore essentially unaffected by any ice I*c* presence.

The dielectric spectra in Fig. 4, show that the loss decreases significantly, and that the loss peak, which could be observed in rHDA, moves to outside the range on the low-frequency side in LDA. Thus, the isothermal results confirm the behavior obtained on isobaric heating (Fig. 2).

The significantly decreasing loss at the rHDA to LDA transition must be due to a large increase of τ. The τ of LDA cannot be obtained with certainty, but even if one accounts for a suppression of the loss peak height by a possible presence of 50% of ice I*c*, superposition of the dielectric spectra in Fig. 4 shows that τ is more than 10 times longer than that of rHDA. The result is very surprising since τ generally increases with increasing density (pressure) at constant temperature. Consequently, the increase of τ at the transition, with a simultaneous density decrease of 25%, must have a structural origin; i.e., the

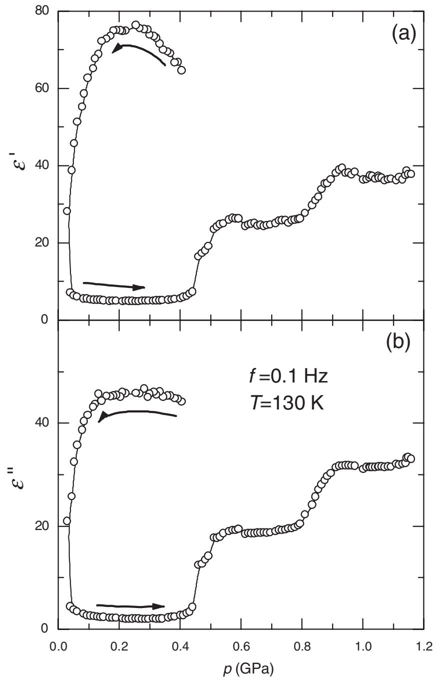

FIG. 3. The dielectric permittivity ε' and loss ε'' at 130 K. The decrease on depressurization shows the rHDA to LDA (and possible ice I*c*) transition, and the two step increase on pressurization shows the reverse transition. The difference in ε' and ε'' for rHDA at 0.4 and 1.15 GPa is due to the pressure induced increase of τ.

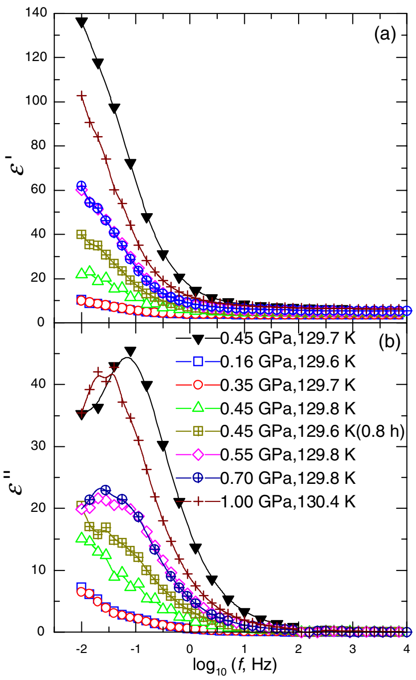

FIG. 4 (color online). The dielectric permittivity ε' and loss ε'' as a function of frequency on depressurization (solid symbol) and subsequent pressurization after the pressure had been decreased to ~0.03 GPa.

change in the local structure must lead to severe restrictions for the dipole motions.

The crystalline ices, ice I*h* and I*c*, exhibit H_2O reorientational freedom at high temperature, and therefore a dielectric relaxation process. (Ices I*c* and I*h* have identical dielectric properties [23].) But in these cases the reorientational motions are restricted by the "ice rules" suggested by Bernal and Fowler [24]. On each bond in the tetrahedrally coordinated ice structure there are two proton sites, and these are occupied according to the rules that there are two protons adjacent to each oxygen and one proton on each bond. This preserves the water molecule but allows also for dynamical disorder in the orientation of the molecule or, equivalently, proton disorder. The ice rules makes a single reorientational H_2O jump forbidden in a perfect lattice since the ice rules would not be preserved, and it therefore requires the involvement of a defect. The relaxation process in ice I is governed by Bjerrum defects [25], i.e., a double occupation protons (Bjerrum *D* defect) or absence of protons (Bjerrum *L* defect) at the two proton sites between two neighboring oxygens. These requirements for the process, which are imposed by the ice rules, increases τ by several orders of magnitude and makes τ dependent on the nature of the samples, where well-purified single crystals have longer τ than impure and polycrystalline samples [23,26]. That is, the ice rules become less effective in limiting the relaxation rate as the number of lattice defects and impurities increases.

The results in Figs. 1 and 2 show that the loss in LDA is larger than that in ice I*c* under similar conditions. Consequently, τ of LDA ice must be in between that of rHDA and ice I*c* (I*h*). The recovery of the ice rules at the rHDA to LDA transition, and the further ordering process at the LDA to ice I*c* transition, which increases the effect on τ caused by the ice rules, explain well the value for τ of LDA in between that for rHDA and ice I.

In summary, τ increases by more than an order of magnitude at the rHDA to LDA transition despite the much decreasing density, which shows that the increase must be associated with the structural change. The recovery of the well-established ice rules offers a convincing explanation for the surprising increase of τ at the transition. These strongly limit the relaxation rates in ices I*c* and I*h*, and are most likely the cause of the restricted dipole mobility also in LDA. This result corroborates those of structural studies, which indicate a local-order similarity between LDA and the crystalline ices I*c* and I*h*, and shows that τ of LDA displays crystallinelike behavior.

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