Experimental Evidence for a Crossover between Two Distinct Mechanisms of Amorphization in Ice *Ih* under Pressure

Thierry Strässle

Laboratory for Neutron Scattering, ETH Zurich and Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

Stefan Klotz and Gérard Hamel

Physique des Milieux Denses, IMPMC, CNRS-UMR 7590, Université Pierre et Marie Curie, FR-75252 Paris, France

Michael M. Koza and Helmut Schober

Institut Laue-Langevin, FR-38042 Grenoble, France
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We report neutron scattering data which reveal the central role of phonon softening leading to a negative melting line, solid-state amorphization, and negative thermal expansion of ice. We find that pressure-induced amorphization is due to mechanical melting at low temperatures, while at higher temperatures amorphization is governed by thermal melting (violations of Born's and Lindemann's criteria, respectively). This confirms earlier conjectures of a crossover between two distinct amorphization mechanisms and provides a natural explanation for the strong annealing observed in high-density amorphous ice.

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The transformation from a crystalline to an amorphous phase has been observed in many solids and is generally referred to as solid-state amorphization (SSA) ([1] and references therein). Among other mechanisms, the transformation into the amorphous state may be induced by irradiation and particle bombardment, or by the application of pressure. Pressure-induced solid-state amorphization (PIA) has been associated with systems exhibiting negative thermal expansion (NTE) [2] and/or with systems exhibiting negative melting lines [3]. In what follows we demonstrate the close link between these three features in the case of ice *Ih* and find their respective origins in the pressure-induced phonon softening characteristic for ice *Ih*.

We have recently measured the phonon dispersion of (deuterated) ice *Ih* to 0.5 GPa using coherent inelastic neutron scattering [4]. With a Born-von-Kármán lattice dynamical model fitted to the data, we found that the entire lower transverse acoustic (TA) phonon branch along the [100] direction (Γ - M) shows dispersionless softening [4]. Extrapolation to higher pressure P shows that an infinite set of phonons with different q vectors freeze out simultaneously. Theory suggests that such behavior constitutes the very origin of PIA in ice and other systems [5,6]. The corresponding mechanism is referred to as amorphization by *mechanical melting* and complies—at the Brillouin zone center—with a violation of Born's stability criteria [7]. It is important to notice that mechanical melting is (i) in reciprocal space, a local process since it involves in the extreme case softening of a single phonon branch, and (ii) is temperature *independent* since the phonon dispersion varies, in general, very little with temperature T . This behavior is in striking contrast to *thermal melting* being a temperature-dependent process, where melting occurs when atoms or molecules are thermally displaced beyond

a critical distance δ_L from their equilibrium positions. This criterion for thermal melting, owing to Lindemann [8] and its generalization [9], have shown to be valid empirically for a wide class of simple solids and are supported by various molecular dynamics calculations [9–12]. Specific to the case of ice *Ih* is the ongoing debate whether PIA in ice should be associated with thermal melting, as originally suggested by Mishima *et al.* [3], or with mechanical melting as had been suggested later [5,13], or if these are competing effects depending on the temperature [13,14]. *In situ* experiments which probe directly the microscopic mechanism governing PIA are still missing. They also bear the key to a better understanding of the nature of the amorphous product, whether it should be considered an ill-crystalline or truly amorphous phase, or even related to the liquid at higher temperatures.

Here we report measurements of the phonon density of states (PDOS) under pressure, carried out at low temperature over the entire stability range of the ice *Ih* structure. Being an integral quantity, the PDOS defines the thermodynamic properties of the system and is hence relevant for *thermal* melting. This approach contrasts with our previous measurements of individual phonon branches [4] which probe mechanical melting. These new data give clear experimental evidence of a crossover from mechanical to thermal melting in the 100 K range.

We have employed incoherent inelastic neutron scattering (IINS) to $P \leq 1.6$ GPa on a nondeuterated powder sample of ice *Ih* (~ 50 mm³) loaded into a Paris-Edinburgh pressure cell equipped with toroidal cubic boron nitride anvils [15]. The cell was cooled by a dedicated cryocooler allowing temperatures down to 4 K [16]. IINS spectra were recorded in neutron energy gain configuration ($E_i = 4.8$ meV) at $T = 80$ K on the time-of-

flight spectrometer IN6 at ILL (France). Pressure was determined within 10% accuracy from applied force and calibration curves known from previous runs with the same experimental setup using a pressure calibrant [17,18]. Since the pressure could be changed *in-situ* at low temperatures, we were able to observe the evolution of the PDOS of ice *Ih* through the transition towards high-density amorphous ice (HDA) at experimental conditions similar to Mishima *et al.*'s first observations [3]. Figure 1 shows spectra of the measured PDOS corrected for the Debye-Waller, $1/\omega$, polarization and thermal population factors only [19]. The PDOS of ice *Ih* peaks at ~ 7 meV, in agreement with previous measurements. Upon pressure increase to ~ 1 GPa the vibrational spectrum is shifted to lower energies as seen by the shift of the Debye tail below ~ 5 meV. Above ~ 1 GPa the ice *Ih* peak at ~ 7 meV decreases in intensity while a new peak at ~ 11 meV gradually develops giving evidence of the formation of HDA. The transformation extends over ~ 0.5 GPa in good agreement with [3] and *in-situ* neutron diffraction studies where pressure is also applied directly onto polycrystalline ice *Ih* [18]. Eventually above ~ 1.5 GPa the sample has completely converted to HDA.

The observed redshift of the low-energy part of the PDOS is obviously due to the pressure-induced softening of TA phonons detected in various measurements previously reported ([4] and references therein). However, softening of a single TA branch does not necessarily result in an overall shift of the PDOS to lower frequencies, since the majority of other phonon branches may exhibit ordinary hardening. The observed effect on the measured PDOS may be compared to what is expected on the basis of the previously applied lattice dynamical model [4], when extrapolated to 1.0 GPa (Fig. 2). The excellent agreement shows that the model accurately parametrizes the pressure dependence of the PDOS over at least ~ 1.5 GPa and confirms that the pressure-induced softening of specific

TA and TO branches dominates the entire low-energy part of the PDOS resulting in an overall shift of the vibrational spectrum below $E \sim 12$ meV to lower frequencies. Note that, in contrast to the calculated PDOS, the measured PDOS is broadened by the instrumental resolution.

With the PDOS and its pressure dependence in hand we are able to derive various thermodynamic quantities such as the specific heat c_p , the lattice entropy S_l , the macroscopic Grüneisen parameter Γ , and the linear thermal expansion coefficient α . In what follows we will show that the softening in the PDOS may also explain the negative melting line ([20] and references therein) and that extends at lower temperatures to the PIA line via thermal melting.

Thermal melting depends on the mean atomic displacements which, owing to the molecular nature of ice, must be replaced by molecular displacements. This quantity can be readily derived from the PDOS $g(E)$ [21]:

$$\langle u^2 \rangle = \frac{\hbar^2}{2M} \int_0^\infty \frac{g(E)}{E} \left(\frac{1 + e^{-\beta E}}{1 - e^{-\beta E}} \right) dE, \quad (1)$$

where M stands for the molecule mass and $\beta = 1/k_B T$. Values of $\langle u^2 \rangle$ from Eq. (1) may be compared to measured values from neutron diffraction at $P = 0$ (Kuhs *et al.* in [20], p. 24) and show very good agreement (Fig. 3). Note, that we restrict our discussion below to the pressure dependence of $g(E)$ only; i.e., the temperature dependence of $\langle u^2 \rangle$ enters indirectly via the thermal population factor only. According to [8,9], melting occurs when

$$\sqrt{\langle u^2 \rangle} / d_{NN} > \delta_L, \quad (2)$$

with d_{NN} the molecular nearest-neighbor distance. Since D_2O ice *Ih* at 1 bar melts at 277 K, we chose $\delta_L \sim 0.088$ to comply with the melting line at $P = 0$ (Fig. 3). This is indeed a physically reasonable value [10], bearing in mind

FIG. 1 (color online). Measured PDOS through the transition from ice *Ih* to HDA at ~ 1 GPa ($T = 80$ K), with features specific for ice *Ih* and HDA marked by the arrows. Note the pressure shifts to lower and higher energies in ice *Ih*, and HDA, respectively.

FIG. 2 (color online). PDOS of ice *Ih* derived from a lattice dynamical model [4] (upper curves) and direct IINS measurements (lower curves, from Fig. 1). The dashed black line approximates measured background contributions from the anvil-gasket assembly, the vertical dashed lines are guides to the eye.

FIG. 3 (color online). Mean molecular displacements reconstructed from PDOS together with mean oxygen displacements determined at $P = 0$ from neutron diffraction (circles) (Kufs *et al.* in [20], p. 24). The horizontal line denotes the Lindemann criterion (see text). Vertical arrows denote conditions where thermodynamic melting is observed at $P = 0$ and expected at $P > 0$, respectively. Inset: PDOS derived from a lattice dynamical model fitted to the measured phonon dispersion at $P = 0$, 0.5 GPa (both $T = 140$ K) and extrapolated PDOS to $P = 1.0$, 2.0 and 2.3 GPa [4].

that Lindemann's criterion may need some adjustments if applied to molecular solids. With this value of δ_L fixed and using the values of $\langle u^2 \rangle$ derived from the measured PDOS at $P > 0$, we derive melting temperatures expected from the variation of the PDOS under pressure (see Fig. 3 and circles in Fig. 4). Specifically, the negative melting curve of ice Ih is readily identified to originate from the red-shift of the PDOS leading to an anomalous increase of $\langle u^2 \rangle$ with pressure [Fig. 3 and Eq. (1)]. We note, however, that the slope of the melting line determined this way is *smaller* than what is found experimentally ([20] and references therein). Hence, our model tends to *overestimate* the critical pressures $P(T)_c^L$ for thermal melting via Lindemann's criterion. Similarly, in our previous study which focused on the PIA at low temperatures [4], we found the critical pressure P_c^B for mechanical melting via Born's criterion being *overestimated* as well (Fig. 4). It is important to note that both Lindemann's and Born's criteria inherently give the upper limits for a perfect homogeneous solid to withstand melting [4,22]. A real solid system anticipates the limits given by these criteria due to defects and surface effects, as has been extensively discussed in the literature ([23,24] and references therein) and demonstrated experimentally by Johari and Anderson [23]. If we scale therefore both $P(T)_c^L$ and P_c^B by the same factor 0.54 to account for these effects as well as the various approximations arising from the Born–von Kármán fit, we find reasonable correspondence with both the experimental melting line of ice Ih at high temperatures and the pressures at which PIA occurs at low temperatures. Of course, this analysis cannot

FIG. 4 (color online). Mechanical (blue line) and thermal (red line) melting in ice. The upper pressure axis corresponds to data points of this work (circles from Fig. 3) and Ref. [4] (blue line, mechanical melting is independent of T , see text). The lower axis corresponds to literature data on the melting line (asterisks, Ref. [20]) and PIA (triangle, Ref. [3]). Paths A and B indicate PIA below and above the crossover temperature, respectively.

be expected to reproduce details of the melting and amorphization curves, such as reported by Mishima [13] based on experiments on emulsified water. However, it provides a fundamental insight into the competing intrinsic mechanisms leading to melting or amorphization in ice: based on the measured PDOS and the variation of the elastic constants, we find that a pressure increase leads to mechanical melting at sufficiently low temperatures (Fig. 4, path A), and to thermal melting at higher temperatures (Fig. 4, path B). This finding is independent of the scaling factor involved.

The crossover temperature between these two mechanisms is thereby dictated by the mean energy of the phonons which show softening (~ 8 meV $\equiv 95$ K) whereas the exact values of the critical pressures of both $P(T)_c^L$ and P_c^B are determined by the respective amount of softening. Apparently, the latter property is less accurately assessable, explaining in part the scaling factor needed to match the experimental and calculated melting lines.

This experimental evidence of a crossover temperature separating two distinct mechanisms of amorphization confirms earlier theoretical [14] and experimental [13] conjectures and reconciles opposed views on the microscopic origins of PIA in ice Ih. The local structure of the amorphous phase produced from mechanical melting is expected to be highly “defective” owing to the manifold of simultaneous lattice-instabilities involved in mechanical melting. On the other hand, the amorphous phase from thermal melting results from exceedingly large (dynamical)

cal) molecular displacements and hence represents *per se* a thermally annealed product. We thus naturally expect that upon warming the amorphous phase obtained by mechanical melting relaxes towards an annealed form similar to the one obtained by thermal melting. Indeed, strong relaxation phenomena have been reported recently ([17] and references therein), when HDA prepared from compression at low temperatures is warmed up at pressures between 0 and 1 GPa. For the general case, we conclude that PIA may be invoked (i) exclusively by mechanical melting, if only a minority of TA branches exhibits dispersionless softening of an entire phonon branch, (ii) exclusively by thermal melting, if a majority of TA and TO branches exhibits overall softening of part of the PDOS without pronounced dispersionless softening of certain TA branches, and (iii) by mechanical and thermal melting, if the very last condition is relaxed. Ice Ih represents an example of the latter case as has been illustrated above. An example of PIA due to mere mechanical melting may be found in the case of THF clathrate hydrate [25,26]. This system shows no NTE in the entire temperature range [27,28], and since NTE requires an overall softening of part of the PDOS, thermal melting may be excluded. In fact, specific TA branches of THF hydrate exhibiting pressure-induced phonon softening are being identified using coherent inelastic neutron scattering [29]. As for silica, PIA at low temperature was shown to be due to mechanical melting ([30] and references therein) and the same may apply for germania and various fourfold-coordinated semiconductors [31]. The lack of data at higher temperatures prevents, unfortunately, determining if there is a similar crossover than found in ice. Finally, the case of PIA due to mere thermal melting may be related to SSA by irradiation or particle bombardment, since this mechanism has been found experimentally to increase the mean atomic or molecular displacements and does not involve specific phonon modes [10]. We thus presume that the astrophysically relevant form of vastly abundant high-density amorphous ice in outer space [32,33] is more closely related to the annealed form of HDA [17] obtained from thermal melting than to the form obtained by mechanical melting.

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