Nature of the Polyamorphic Transition in Ice under Pressure

S. Klotz,[1,*] Th. Strässle,[1] R. J. Nelmes,[2] J. S. Loveday,[2] G. Hamel,[1] G. Rousse,[1] B. Canny,[1]
J. C. Chervin,[1] and A. M. Saitta[1]

[1]*Physique des Milieux Denses, IMPMC, CNRS-UMR 7590, Université Pierre et Marie Curie, F-75252 Paris, France*
[2]*School of Physics and Centre for Science at Extreme Conditions, The University of Edinburgh, Edinburgh EH9 3JZ, United Kingdom*

(Received 5 August 2003; published 19 January 2005)

We present a neutron diffraction study of the transition between low-density and high-density amorphous ice (LDA and HDA, respectively) under pressure at ~0.3 GPa, at 130 K. All the intermediate diffraction patterns can be accurately decomposed into a linear combination of the patterns of pure LDA and HDA. This progressive transformation of one distinct phase to another, with phase coexistence at constant pressure and temperature, gives direct evidence of a classical first-order transition. *In situ* Raman measurements and visual observation of the reverse transition strongly support these conclusions, which have implications for models of water and the proposed second critical point in the undercooled region of liquid water.

DOI: 10.1103/PhysRevLett.94.025506 PACS numbers: 62.50.+p, 61.12.Ld, 61.25.Em, 61.43.–j

Water exists at low temperatures in two amorphous forms, low- and high-density amorphous ice (LDA and HDA). LDA can be transformed into HDA at pressures of ~0.6 GPa at 77 K [1] and ~0.3 GPa at 130 K [2]; and, at 130 K, HDA can be transformed back to LDA at ~0.05 GPa [2]. The transition appears abrupt in volumetric measurements and, as noted, is reversible with hysteresis at 130 K. On this basis it was interpreted as a classical, first-order transition between two distinct phases [1,2]. This conclusion is important for our understanding of amorphous ice in relation to liquid water and, consequently, for models which were introduced to explain the unusual thermodynamic properties of water [3]. Some simulations suggest that LDA and HDA are essentially the glassy forms of high- and low-density water which appear as separate phases below a second critical point C' (see Fig. 1), located in the undercooled region of the liquid [3,4]. The existence of such a critical point is controversial, and other calculations indicate that HDA is a "mechanically collapsed" ice I*h* [5], not related to the liquid. In either case, the understanding of the nature of the transition between LDA and HDA is crucial in the current water debate and continues to be disputed [6–9].

The matter remained uncertain in the absence of any microscopic characterization of the sample through the transition. Mishima *et al.* have observed a sharp boundary in LDA compressed in an ungasketed diamond anvil cell [10] which they identified on the basis of Raman spectra as the LDA to HDA transition. But the pressure gradients inherent in this experiment meant that the possibility of a continuous transition could not be ruled out. In view of the experimental difficulty of *in situ* characterization, all subsequent attempts to clarify the detailed nature of the transition have instead been carried out on samples recovered to ambient pressure, where the (irreversible) conversion of HDA to LDA occurs at ~105–115 K over a time scale of minutes to hours. From such experiments two conflicting views have recently emerged. Neutron and x-ray diffraction measurements by Tulk *et al.* [6] and Guthrie *et al.* [7] have been interpreted as showing a continuous structural relaxation of HDA to LDA with intermediate states that cannot be understood as mixtures of the two pure phases. Such a conclusion appears inconsistent with the existence of a second critical point [3,4,11]. In contrast, new work by Mishima *et al.* [8] based on Raman scattering and visual observation concludes that the ambient-pressure transition is indeed discontinuous, with nucleation and phase coexistence. And in subsequent neutron diffraction studies very similar to those in Refs. [6,7], Koza *et al.* [9] have come to the conclusion that the data can indeed be interpreted as a phase mixture, provided the correct end members are chosen, i.e., annealed HDA and LDA. But all these studies have the common drawback that their significance for the current water debate is limited since they do not probe the equilibrium phase boundary between LDA and HDA, estimated to be at ~0.2 GPa [2,12]. Instead they probe the kinetically activated irreversible conversion of HDA outside its *P*-*T* range of stability, in a temperature range (105–115 K) where HDA also changes significantly through annealing processes. A structural characterization under *in situ* conditions is required.

In this Letter we report neutron diffraction studies which, unlike all previous studies since Ref. [2], are carried out as a function of pressure, at a relatively high temperature of 130 K (Fig. 1), where the transition is reversible [2] and not obscured by relaxation phenomena. We also report *in situ* Raman measurements and visual observations under the same conditions. In contrast to previous studies at atmospheric pressure and variable temperature, the experiments reported here are able to probe the LDA-HDA phase boundary [1,2] with both phases in equilibrium.

The experiments were carried out at the PEARL station of the ISIS Facility of the Rutherford Appleton Laboratory at Chilton, U.K., using the Paris-Edinburgh press [13,14]. Approximately 100 mm^3 of water (D_2O, 99.96%) were loaded into the cell, cooled to 100 K to give ice I*h*, and

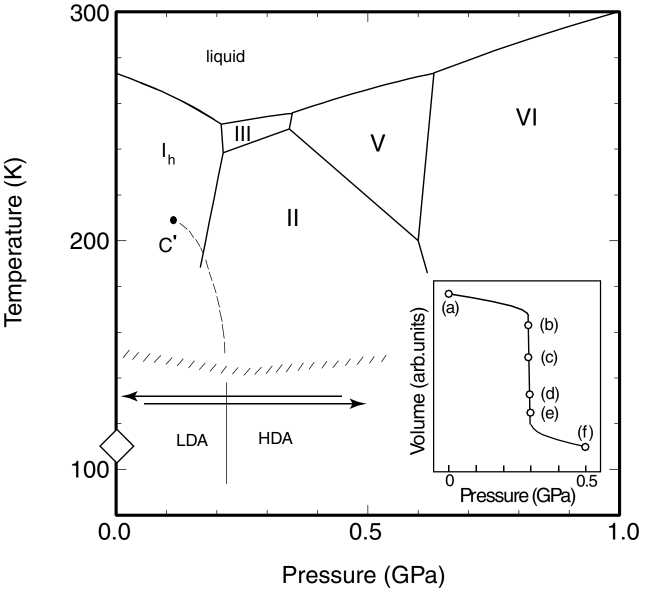

FIG. 1. Main figure (adapted from Refs. [2–4]). Phase diagram of water at low temperatures indicating schematically the equilibrium LDA-HDA phase boundary estimated to be at ~0.2 GPa in the absence of hysteresis [2,12], which may terminate in the hypothesized second critical point C′. The open diamond indicates the temperature range in which the thermally activated transformation of HDA to LDA occurs in warming HDA samples at ambient pressure [6–9], and the two arrows mark the paths of our neutron and Raman measurements. The recrystallization zone of amorphous ice is shown by the hatched area. Inset: The phase transition at 130 K in terms of sample volume with increasing pressure, as found by Mishima *et al.* [2]. The circles marked (a)–(f) approximately locate the conditions where patterns (a)–(f) of Fig. 2 were taken.

compressed at this temperature to ~1.5 GPa to produce pure HDA. The sample was then decompressed to atmospheric pressure and heated to 130 K where it transformed to pure LDA. Diffraction data were collected at 130 K as the sample volume was successively decreased (the parameter that is directly controlled in our experiments is the volume of the sample rather than the pressure). The patterns were corrected for the wavelength-dependent attenuation of the sintered diamond anvils [15].

Figure 2 shows diffraction patterns from the initial LDA, four intermediate volumes through the transition, and the final HDA. The shift of the main diffraction feature at 3.7 Å shows that LDA compresses detectably between 0 GPa and the start of the transition [patterns (a) and (b)]. On further reduction of volume, the positions of the main features at 3.7 Å (LDA) and 3.05 Å (HDA) then remain essentially constant while their intensities reverse through the transition [patterns (b)–(e)]. Finally, HDA compresses after completion of the transition [patterns (e) and (f)], with the pressure dependence observed on pure samples of HDA [13]. Although it is not possible in our experiment to determine the absolute value of the pressure through an independent pressure marker, it can be estimated from known pressure-load curves and from the position of the main HDA peak. The peak positions in patterns (b)–(e) are consistent with the transformation of LDA to HDA at a constant pressure of ~0.3 GPa through the transition, as determined in Ref. [2] at 130 K.

To investigate the changes through the transition further, the diffraction patterns of pure HDA and LDA were first parametrized by fitting with a convenient function—a superposition of Gaussians—as shown in Fig. 2, to give I_L as a fit to the LDA pattern and I_H as a fit to the HDA pattern. The inset to Fig. 2 shows that the main peaks are significantly different in shape and width, as well as in position in d spacing (or Q). The intermediate diffraction patterns [(b) to (e)] were then fitted with a superposition of these two forms:

$$I(d) = \eta I_L(d/r_L) + (\eta - 1) I_H(d/r_H). \tag{1}$$

where the only fitting parameters are the phase fraction of the two forms (η) and two peak-shift parameters (r_L and r_H) which take account of the fact that the pure forms in (a) and (f) are at slightly different pressures from those in mixed-phase patterns. As shown by the fits, patterns (b) to (e) can all be exactly decomposed into a mixture of pure HDA and LDA, and the peak-shift parameter for HDA remains constant throughout, confirming that the transition to HDA occurs at a constant pressure. There is a slight change in the LDA peak position from panels (b) to (e), attributable to (small) initial pressure gradients being reduced to zero as the LDA is all progressively compressed up to the transition pressure—causing a small shift in the average pressure of the LDA component.

These results are all characteristic of a transformation of one homogeneous phase to another through a discontinuous transition, with phase coexistence at a constant pressure and temperature. Any other interpretation is extremely implausible: the initial LDA and final HDA are unambiguous in our data, and a continuous transition would require all the intermediate states of the sample to give patterns accidentally identical to linear combinations of these initial and final forms, over a wide Q range and over a density change of ~20%, and to high precision.

The microscopic behavior of our sample through the abrupt volume change [1,2] is clearly as expected for a first-order transition, and it would be desirable to demonstrate the same for the reverse transition from HDA to LDA. However, this occurs at a low pressure of ~0.06 GPa [2] where it is difficult to control the pressure cell used for our neutron diffraction studies. Instead, the coexistence of the two different amorphous phases during the reverse transformation was confirmed by complementary *in situ* Raman and visual observations at the same temperature as the neutron measurements. HDA was obtained by compressing ice H_2O phase I*h* at 80 K to 2.2 GPa in a membrane diamond anvil cell. The temperature was then increased to 130 K, and measurements were taken with decreasing pressure at this temperature. The pressure was measured using the ruby fluorescence scale (corrected for the temperature shift) and the Raman spectra were recorded using a DILOR XY triple monochromator with an Ar-ion laser operated at a wavelength of 514.5 nm. A beam size of less than ~5 μm allowed spectra to be collected with high spatial resolution at various points of the sample chamber of ~270 μm diameter. Different values of the laser power were found to have no influence on the spectra. Above 0.3 GPa the sample appeared homogeneous, from both visual appearance and Raman spectra taken at different locations inside the gasket hole (Fig. 3). The Raman spectrum of the O-H stretching band with two broad features centered at ~3140 and 3400 Å identifies HDA, by comparison with published data at ambient [8] and high pressure [16]. On decreasing the pressure well below 0.3 GPa, irregular dark lines appeared across the whole sample and became sharper and broader over a time scale of an hour. A scan (Fig. 3) shows a strong increase in the intensity of the feature located at 3140 Å when the laser probes the middle of a line, and this is characteristic of pure LDA [8,17], by comparison with known LDA spectra at ambient pressure [18]. Crystalline phases can be excluded, since their spectra in this frequency region have sharp features and their intensities are significantly different [17].

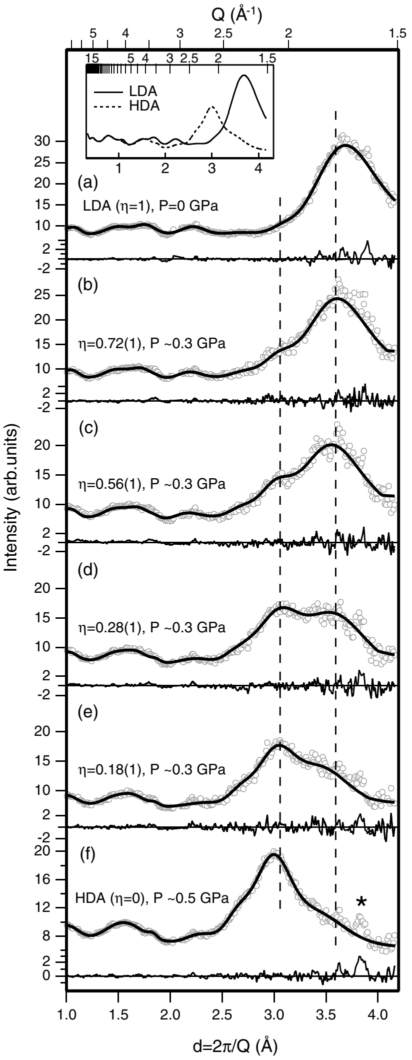

FIG. 2. Neutron diffraction patterns taken as LDA ($\eta = 1$; top) transforms to HDA ($\eta = 0$; bottom) under reducing sample volume at 130 K. The acquisition time was ~2 h for each data set. The lines through the data (circles) of patterns (a) and (f) are parametrizations of the pure LDA and HDA patterns, respectively. These are shown together without the measured data in the inset. The scales on the inset are Q (Å^{-1}) (top) and d (Å) (bottom). The "intermediate" samples [patterns (b)–(e), $0 < \eta < 1$] can be fitted (line) to a linear combination of the pure LDA and HDA patterns at a constant pressure, as explained in the text. Difference curves are given below each pattern. The asterisk in panel (f) marks a peak from a small amount of untransformed ice I*h* that is equally present in all the patterns within statistics and was excluded from the fits.

This first *in situ* diffraction and optical study of the LDA-HDA transition resolves the conflicting conclusions from various recent experiments on the thermally activated transition at ambient pressure [6–9]. Our results provide

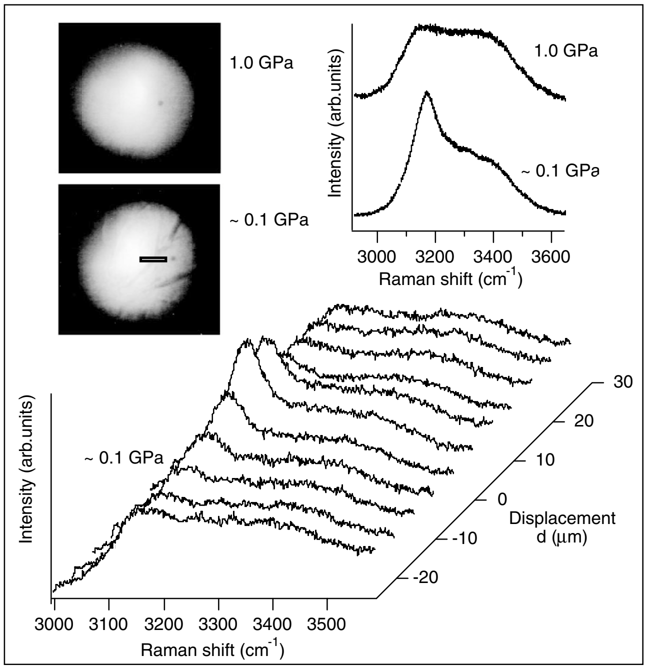

FIG. 3. Microphotographs and corresponding Raman spectra showing the appearance of a phase mixture of HDA and LDA at 130 K as a function of decreasing pressure, in a diamond anvil cell. Upper left: pure HDA at 1.0 GPa; below: LDA (dark lines) and HDA (bright background) at ~0.1 GPa. Upper right: Raman spectra taken from pure HDA at 1.0 GPa and from a dark line (LDA) at ~0.1 GPa. Lower: sequence of Raman spectra taken along the black line (crossing a dark line of LDA) indicated in the ~0.1 GPa picture.

compelling direct evidence for a discontinuous transition between two distinct amorphous forms [19], as first suggested from volumetric measurements [1,2]. The disputed structural changes reported in HDA at ambient pressure on warming towards the transformation [6,7,9] are likely to arise from a progressive annealing of HDA rather than the formation of distinct, stable states intermediate between HDA and LDA [8]. In any case, as said, this ambient-pressure behavior is not directly relevant to the key issue of a possible second critical point.

Although the first-order character of the *in situ* transformation is beyond reasonable doubt from our findings, they cannot prove the existence of a second critical point, since they are confined to the solid region of amorphous water. However, the results clearly show experimental behavior that tends to support this intriguing possibility. Phase separation below a critical point in undercooled liquid water is predicted by widely used water potentials, such as ST2 [4], TIP4P [11], and TIP5P [20]. More recent work even indicates the possibility of multiple liquid-liquid transitions in ST2 water [21]. In these scenarios the liquid-liquid transition line naturally extends to low temperatures to meet the LDA-HDA transition line, which would produce a behavior as seen in our experiments. In contrast, singularity-free models, such as in Refs. [22–24], are difficult to reconcile with our results, since these models predict a continuous transition. Our structural data thus constrain any water model that aims for a comprehensive understanding of both liquid and solid (amorphous) forms, and provide a basis for further theoretical studies of the behavior of water at low temperatures. The contrast between the clarity of the behavior under pressure at 130 K and the uncertain conclusions to be drawn from the ambient-pressure studies at lower temperatures indicates that further studies need to be conducted under *in situ* conditions at temperatures high enough to overcome annealing effects.

It is interesting to note that our diffraction and Raman data were collected at a temperature (130 K) close to the reported glass transition temperature (T_g) of LDA, of hyperquenched and vapor deposited water [25], and of HDA, i.e., 129–140 K [26] at 0 GPa, and only a little below an estimated T_g of 150 K for HDA at 0.3 GPa [26]. But the effective T_g in our experiments would be lower than these estimates, because the time scale of the neutron and Raman measurements is 10^4 s, which is 2 orders of magnitude longer than the time scale normally used to define T_g [27]. Thus, there is a possibility that our measurements may in fact probe the domain of "ultraviscous water" [3].

This work was funded by the Swiss National Science Foundation (T. S., Grant No. 81EZ-68588) and a research grant from EPSRC (J. S. L. and R. J. N.), and is supported by CCLRC through access to beam time and other resources. We are grateful for helpful discussions with M. E. Cates, W. C. K. Poon, M. M. Koza, D. D. Klug, and C. A. Tulk.

---

*Electronic address: stk@pmc.jussieu.fr

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

[2] O. Mishima, J. Chem. Phys. **100**, 5910 (1994).

[3] O. Mishima and H. E. Stanley, Nature (London) **396**, 329 (1998).

[4] P. H. Poole *et al.*, Nature (London) **360**, 324 (1992).

[5] J. S. Tse, J. Chem. Phys. **96**, 5482 (1992).

[6] C. A. Tulk *et al.*, Science **297**, 1320 (2002).

[7] M. Guthrie *et al.*, Phys. Rev. B **68**, 184110 (2003).

[8] O. Mishima and Y. Suzuki, Nature (London) **419**, 599 (2002).

[9] M. M. Koza *et al.*, J. Phys. Condens. Matter **15**, 321 (2003).

[10] O. Mishima, K. Takemura, and K. Aoki, Science **254**, 406 (1991).

[11] H. Tanaka, J. Chem. Phys. **105**, 5099 (1996).

[12] E. Whalley, D. D. Klug, and Y. P. Handa, Nature (London) **342**, 782 (1989).

[13] S. Klotz *et al.*, Phys. Rev. Lett. **89**, 285502 (2002).

[14] S. Klotz *et al.*, Z. Kristallogr. **218**, 117 (2003).

[15] R. M. Wilson *et al.*, Nucl. Instrum. Methods Phys. Res., Sect. A **354**, 145 (1995).

[16] R. J. Hemley, L. C. Chen, and H. K. Mao, Nature (London) **338**, 638 (1989).

[17] B. Minceva-Sukarova, W. Sherman, and G. Wilkinson, J. Phys. C **17**, 5833 (1986).

[18] The exact peak positions of LDA and HDA depend on both pressure and temperature, as well as the state of annealing, as shown in Ref. [17] and in O. Mishima and Y. Suzuki, J. Chem. Phys. **115**, 4199 (2001).

[19] Our measurements refute the conclusions reached on indirect grounds by Johari and Andersson [J. Chem. Phys. **120**, 6207 (2004)] in work published while this Letter was in review.

[20] M. Yamada *et al.*, Phys. Rev. Lett. **88**, 195701 (2002).

[21] I. Brovchenko, A. Geiger, and A. Oleinikova, J. Chem. Phys. **118**, 9473 (2003).

[22] H. E. Stanley and J. Teixeira, J. Chem. Phys. **73**, 3404 (1980).

[23] A. Geiger and H. Stanley, Phys. Rev. Lett. **49**, 1749 (1982).

[24] S. Sastry *et al.*, Phys. Rev. E **53**, 6144 (1996).

[25] G. P. Johari, A. Hallbrucker, and E. Mayer, Science **273**, 90 (1996).

[26] O. Mishima, J. Chem. Phys. **121**, 3161 (2004).

[27] The time scale is much longer than in recent simulations of the LDA-HDA transition [N. Giovambattista, H. E. Stanley, and F. Sciortino, Phys. Rev. Lett. **91**, 115504 (2003)], which was also not extended above 77 K. The authors note that even a glass may then sample the same structural configurations as the liquid.