

Structure of High-Density Amorphous Ice by Neutron Diffraction

M. A. Floriano and Edward Whalley

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A0R6

and

E. C. Svensson and V. F. Sears

Atomic Energy of Canada Limited, Chalk River Nuclear Laboratories, Chalk River, Ontario, Canada K0J1J0

(Received 21 August 1986)

The static structure factor and pair distribution function of high-density amorphous D₂O ice, which is made by apparently melting ice I at 10.5 kbar and 77 K, have been determined by neutron diffraction at 17 K and zero pressure. The pair distribution function, scaled to 10 kbar, is compared with the same function for D₂O liquid at 9.8 kbar and 321 K. The functions are very similar, which suggests that the structure of the high-density amorph is very similar to that of the, as yet hypothetical, glass that would be obtained by the quenching of water of 10 kbar.

PACS numbers: 61.60+m, 61.40.+b

Ice I undergoes a sharp, apparently first-order, transformation at 77 K and 10 kbar¹ to a high-pressure amorphous phase having a density of 1.31 g cm⁻³ at 10.5 kbar. The transformation occurs on the melting line of ice I extrapolated to low temperatures and appears to be a melting transformation except that the "melt" is a glass. The new phase can be recovered at atmospheric pressure, apparently unchanged except for an elastic expansion to a density of 1.17 g cm⁻³. It is metastable at low pressure, and, when heated,¹⁻³ transforms gradually to amorphs having lower density, and eventually to a low-density amorphous phase similar to that made by condensation of water vapor onto a cold surface.

When the low-density amorph is squeezed at 77 K it also transforms, in what again appears to be a first-order transformation, to a high-density amorph that closely resembles that made by a squeezing of ice I.⁴ In one of these new types of transformation a crystal "melts" below the glass-transition temperature of the melt to a high-density amorphous solid, and in the other a low-density amorphous solid appears to "melt" in a similar way. These transformations have provided us with many new amorphous phases of ice, and both the transformations and the phases are being studied in several ways.^{5,6}

Since the high-density amorph is made on the extrapolated melting line of ice I by a transformation that resembles melting, a question that immediately arises is how the amorph at 77 K and 10 kbar is related to the liquid at higher temperatures. Ideally, to investigate this relation, high-pressure water should be quenched fast enough to form a glass. The liquid at ambient pressure has been so quenched,^{7,8} but only in micron-sized droplets, and it may not be easy to cool it fast enough under pressure. However, the specific volume of the high-density amorph at 10 kbar and 77 K appears to be compatible with the specific volume of liquid water at the

same pressure in the range 300–350 K, and with the specific volume of the liquid on the liquid-I line in the range 251–273 K.¹ This suggests that the phases are directly related. More concrete information on the relation may be obtained by comparison of the pair distribution functions of liquid water and the high-density amorph at similar pressures. This Letter reports a neutron-diffraction determination of the static structure factor and pair distribution function of high-density amorphous D₂O ice at 17 K and zero pressure. The pair distribution function, after scaling to 10.5 kbar and 77 K by means of the estimated compression and thermal expansion, is strikingly similar to that of liquid D₂O at 9.8 kbar and 321 K.⁹

The sample was a wafer about 1.5 mm thick and 69.5 mm in diameter. To make it, a sample of D₂O ice I sandwiched between steel plates lined with Teflon sheets and held in by cadmium and beryllium-copper rings was placed in a piston-cylinder apparatus, cooled in liquid nitrogen, and squeezed to 13 kbar in a hydraulic press. The transformation was very sharp if the pressure was increased slowly. The sample was then removed from the pressure vessel under liquid nitrogen and sandwiched between two disks of single-crystal silicon, and the sandwich was placed in an aluminium holder covered with a cadmium mask in order to restrict to a 50×50-mm square the part of the sample that scatters neutrons. The assembly was then mounted at 77 K in a Displex closed-cycle refrigerator, surrounded by an aluminium radiation shield, and cooled to 17 K. The temperature was measured to ±1 K by two silicon diodes mounted on the top and bottom parts of the holder. The sample temperature was measured continuously during the transfer to the Displex and did not rise above 78 K.

The neutron-diffraction experiments were carried out with the N5 spectrometer at the NRU reactor of Chalk River. A beam of 0.8979-Å neutrons was obtained from

the (110) planes of a beryllium crystal, and during the measurements the plane of the sample bisected the angle between the incident and scattered beams. The total scattered intensity was measured at angles from 2° to 116° in steps of 0.2° . The beam was collimated before and after the sample to 0.55° and 0.59° , respectively. Typically, the principal peak of the diffraction pattern had a height of ~ 25000 counts. The intensity from the empty vessel at 17 K was 100–500 counts except at angles $\lesssim 5^\circ$, where the fast-neutron background rose rapidly, and in the powder peaks from the aluminium radiation shield. This scattering was multiplied by a shielding factor of ~ 0.9 , which was adjusted slightly so as to remove the aluminium powder peaks in the original spectrum, and subtracted from the spectrum with the ice present. The data were corrected for absorption, multiple scattering, and inelastic scattering.¹⁰ The final structure factor $S(q)$, where q is the momentum transferred to the sample, was normalized to the structure factor extrapolated to large momentum transfer, i.e., to $S(\infty) = \sum_a b_a^2 / (\sum_a b_a)^2 = 0.334$, where b_a is the coherent scattering length of nucleus a , and the sum is over all the nuclei. It was extrapolated smoothly to the theoretical value of ~ 0 at $q = 0$, and is plotted in Fig. 1.

The pair distribution function $g(r)$, where r is the distance from the central atom, was calculated from the structure factor via the relation

$$g(r) = 1 + \frac{1}{2\pi^2\rho r} \int_0^\infty q [S(q) - S(\infty)] \sin(qr) dq, \quad (1)$$

where ρ is the number density of nuclei. Numerical integrations were done by the method of overlapping parabolas,¹¹ and spurious ripples were eliminated by a truncation method.¹² The pair distribution function was scaled to 10.5 kbar by division of the distances by the

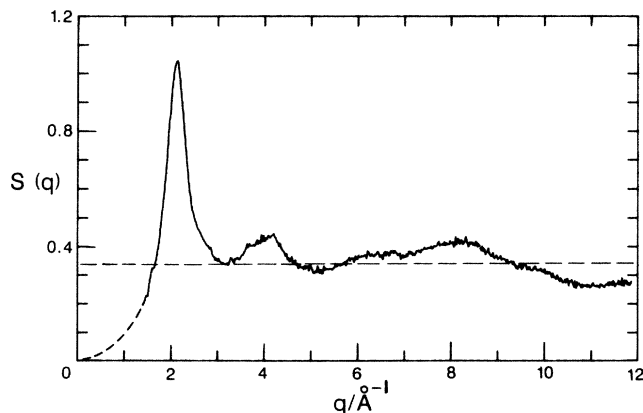


FIG. 1. Static structure factor $S(q)$, where q is the momentum transfer, of high-density amorphous D_2O ice at 17 K and zero pressure. The dashed line represents $S(\infty)$, which is 0.334.

cube root of the relative volume at zero and 10.5 kbar, i.e., by $1.038^{1/3}$; no adjustment was needed to scale it to 77 K.¹³ This scaling is accurate for O-O distances, but, because the force constant for the O—D bond is about 30 times that for the O—O bond, it is quite inaccurate at small distances. The scaled pair distribution function is plotted as the solid curve in Fig. 2. For $r < 0.7 \text{ \AA}$ it is unreliable because errors in the structure factor that are almost independent of the momentum transfer produce a spurious peak near the origin. The pair distribution function of liquid water at 9.8 kbar and 321 K, where the density is 1.21 g cm^{-3} ,¹⁴ is plotted as the dashed line in Fig. 2.

The first peak, at 0.97 \AA in the unscaled spectra, is the intramolecular O—D correlation.⁹ The second peak is the hydrogen-bonded D-O and intramolecular D-D distribution, which have weights of 2 and 1, respectively, and is centered at 1.7 \AA in the high-density amorph. The D-D distance should be little affected by pressure, and so the scaling decreases its value too much.

The third peak, at 2.35 \AA , is caused by the intermolecular D-D distribution in the configuration O—D—O—D. It is well resolved and rather prominent in crystalline ice¹⁵ and in low-density amorphous ice¹⁶ and forms a distinct shoulder in the high-density amorph. In the liquid, the 1.7- and 2.35-\AA peaks appear to merge to form the broad feature at 2.0 \AA , probably partly because thermal excitation makes the intermolecular distances cover broader ranges in the liquid at 321 K than in the solid at 77 K. In addition, the peaks in the apparent distribution function of the liquid are broader than those of the solid, in part because the instrumental resolution, which is $2\pi/q_{\text{max}}$, where q_{max} is the maximum momentum transfer, is 0.70 and 0.53 \AA for the liquid and solid,

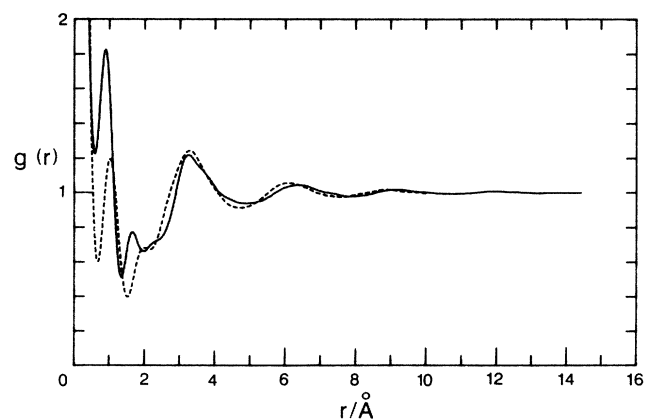


FIG. 2. Pair distribution function $g(r)$, where r is the distance from the central atom, of high-density amorphous D_2O ice at 77 K and 10.5 kbar (solid line) obtained by scaling of the measurements at 17 K and zero pressure, as is described in the text, and pair distribution function of liquid D_2O at 9.8 kbar and 321 K (dashed line) from Ref. 9.

respectively. It follows that the orientational correlation of first neighbors in the high-density amorph at 77 K is substantially increased from what it is in the liquid at 9.8 kbar and 321 K, probably because cooling greatly reduces the number of accessible configurations. This correlation is, however, weaker than in the low-density amorph, both that made by condensation of the vapor¹⁶ and that made by heating of the high-density amorph,¹⁷ presumably because the hydrogen bonds must bend to produce the high density.

A strong peak occurs at 3.36 Å. The peak is similar to the corresponding peak in the liquid, but is a little narrower, probably because the thermal excitation is lower, and has a shoulder at larger separation. It contains several distributions,⁹ but, nevertheless, the coincidence of the corresponding peaks in the liquid and the amorph indicates that their structures are similar, at least out to first- and second-neighbor molecules.

Corresponding weak peaks occur in both samples at ~6.1 and 9 Å and there is also a very weak peak at ~12 Å in the high-density amorph. Each contains many distributions, but the peaks are remarkably similar in position and amplitude in the two phases.

The most striking feature of Fig. 2 is the similarity of the pair distribution functions of the high-density amorph and the liquid. The peaks are sharper in the amorph, no doubt because the decreased thermal excitation between 321 and 77 K greatly reduces the variety of configurations that contribute significantly, and there are small differences in position. The similarity of the pair distribution functions is consistent with the two materials being related as a liquid and the glass obtained by a cooling of it. This supports the suggestion¹ that the transformation of ice Ih to the high-density amorph is analogous to melting.

Bosio, Johari, and Teixeira⁶ have suggested that the high-density amorph may not have the same structure as the glass that is made by quenching of the liquid at atmospheric pressure. It would, in fact, be strange if it had because the two phases differ in density by ~25%

and so must have coordination numbers that differ by ~25%.

We thank G. E. McLaurin for help in the preparation of the samples, B. M. Powell for assistance in the early stages of the measurements, and H. F. Nieman, J. C. Evans, D. C. Tennant, and A. H. Hewitt for technical assistance.

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

²D. D. Klug, O. Mishima, and E. Whalley, *Physica* (Amsterdam) **139 & 140B**, 475 (1986).

³Y. Paul Handa, O. Mishima, and E. Whalley, *J. Chem. Phys.* **84**, 2766 (1986).

⁴O. Mishima, L. D. Calvert, and E. Whalley, *Nature* (London) **314**, 46 (1985).

⁵Edward Whalley, Osamu Mishima, J. Paul Handa, and D. D. Klug, *Ann. N. Y. Acad. Sci.* (to be published).

⁶L. Bosio, G. P. Johari, and J. Teixeira, *Phys. Rev. Lett.* **56**, 460 (1986).

⁷J. Dubochet, M. Adrian, and R. H. Vogel, *Cryo-Lett.* **4**, 233 (1983).

⁸E. Mayer and P. Bruggeller, *J. Phys. Chem.* **87**, 4744 (1983).

⁹A. Y. Wu, E. Whalley, and G. Dolling, *Mol. Phys.* **47**, 603 (1982).

¹⁰G. Placzek, *Phys. Rev.* **86**, 377 (1952).

¹¹R. E. Jones, "Approximate Integrator of Functions Tabulated at Arbitrarily Spaced Abscissas," SC-M-69-335, Sandia Laboratories, 1969 (unpublished).

¹²E. Lorch, *J. Phys. C* **2**, 229 (1969).

¹³E. Whalley, in *Physics and Chemistry of Ice*, edited by E. Whalley, S. J. Jones, and L. W. Gold (Royal Society of Canada, Ottawa, 1973), p. 73.

¹⁴From run 1977A of Ref. 9.

¹⁵S. W. Peterson and H. A. Levy, *Acta Crystallogr.* **10**, 70 (1957).

¹⁶M. R. Chowdhury, J. C. Dore, and J. T. Wenzel, *J. Non-Cryst. Solids* **53**, 247 (1982).

¹⁷M. A. Floriano, E. Whalley, E. C. Svensson, and V. F. Sears, to be published.