

RECENT WORK ON HIGH-DENSITY AMORPHOUS ICE<sup>(1)</sup>

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**Résumé** - La transformation de la glace I<sub>h</sub> en glace amorphe de haute densité à 77 K et 10 kbar se produit à une pression qui est constante avec une précision expérimentale de  $\pm 5$  bars et semble ainsi être une transformation du premier ordre et aussi une nouvelle forme de fusion. Quelques aspects de la structure de la phase amorphe de haute densité ont été déterminés à partir du spectre Raman des oscillateurs O-H et O-D non couplés qui indique les longueurs des liaisons hydrogène O-H...O et par la fonction de distribution radiale pondérée obtenue par diffraction de neutrons. La phase amorphe de haute densité semble être proche du liquide à haute température et à la même pression.

**Abstract** - The transformation from ice I<sub>h</sub> to high-density amorphous ice at 77 K and 10 kbar occurs at a pressure that is constant to the experimental precision of  $\pm 5$  bar, and so seems to be a first-order transformation, and so to be a new kind of melting. Some aspects of the structure of the high-density amorph have been determined from the Raman spectrum of the uncoupled O-H and O-D oscillators, which tells about the hydrogen-bonded O-H...O distances, and from the neutron-weighted radial distribution function. The high-density amorph seems to be closely related to the liquid at higher temperatures and the same pressure.

## I - INTRODUCTION

When ice I<sub>h</sub> is squeezed at 77 K to its extrapolated melting pressure of  $\sim 10$  kbar it undergoes what appears to be a sharp transformation to a high-density amorphous phase, whose density is  $1.31 \text{ g cm}^{-3}$  at 10 kbar and  $1.17 \text{ g cm}^{-3}$  at low pressure [1]. The specific volume of the new phase at 10 kbar and the specific volume of liquid water at the same pressure in the range 300-350 K appear to be on a single line [1], which suggests that the two phases are related, approximately as a liquid and its glass. When the high-density amorph is heated from 77 K at low pressure, it slowly relaxes its structure until the temperature reaches  $\sim 120$  K, where it transforms to a low-density ( $0.94 \text{ g cm}^{-3}$ ) amorphous form [2]. When this low-density amorph is squeezed at 77 K, it also transforms, at  $\sim 6$  kbar, to a high-density amorph that resembles the phase made by transforming ice I at 10 kbar [3].

This paper reviews recent work on these transformations and the phases they produce. In particular, the change of pressure with volume during the transformation of ice I<sub>h</sub> to the high-density amorph has been followed accurately, the Raman spectrum of the uncoupled O-H and O-D oscillators has been measured and converted to the distribution of O...O distances, and the structure factor as measured by neutron diffraction has been converted to the neutron-weighted radial distribution function.

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An obvious question is: what is the relation between the high-density amorph and the liquid at 10 kbar and 300 K? In particular, could the two phases be related as the glass and the liquid that it is made from by rapid quenching? This question will be answered as best we can.

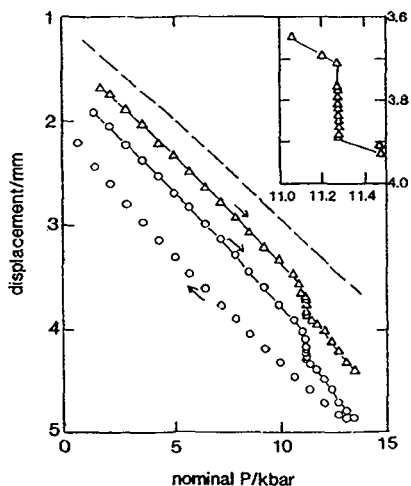


Fig. 1. Displacement of the piston during the transformation of ice Ih to the high-density amorph at 77 K plotted against the nominal pressure, which is calculated without allowing for friction in either the pressure cell or the hydraulic jack that drives the press. Two separate runs are denoted by o and  $\Delta$ .

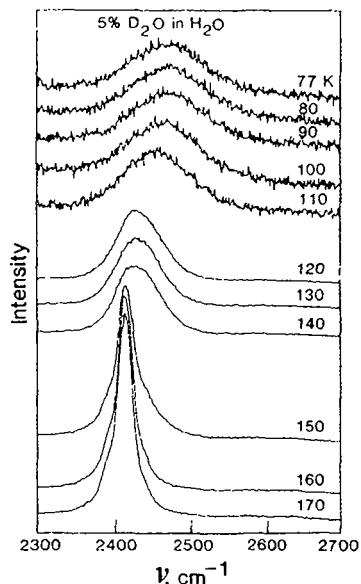


Fig. 2. Raman spectrum at  $\sim 12$  K of the uncoupled O-D vibrations of high-density amorphous ice and the phases made by heating it in succession to the temperatures attached to the curves and held there for 5 min.

## II - NATURE OF THE CRYSTAL-AMORPH TRANSFORMATION

The original measurements of the pressure and volume through the transformation [1] showed that the transformation was sharp enough that it appeared to be of first order, but they were not precise enough to prove it. Since then, thin samples of the high-pressure amorph having a diameter of 70 mm have been made in a piston-cylinder apparatus for experiments by neutron diffraction [unpublished]. The change of volume with pressure for one sample, when  $\sim 8$  min was allowed for equilibrium to be reached after each pressure change, is plotted in Fig. 1. The transformation occurs at a pressure that is constant to the precision of the pressure gauge, which is  $\pm 5$  bar [unpublished]. The transformation seems sharp enough to be first order. If it were a relaxation, the activation volume would have to be of the magnitude of  $\sim 1$  L mol $^{-1}$ , and it seems unlikely that so much cooperative motion can occur at such low temperatures in such a brittle solid.

This transformation of a crystal to an amorphous solid appears, therefore, to be thermodynamically of first order and so seems to be exactly analogous to the melting of a crystal to its fluid. The principal difference between the phenomena described here and melting seems to be that in these experiments the melting occurs below the glass transition of the melt. The only simple explanation of the nature of the transformation is that it occurs by an instability at the surface of the crystal, which is the usual mechanism of melting. The transformation is not experimentally reversible, as seen in Fig. 1, probably because nuclei of the crystal form much too slowly at these low temperatures.

Further experiments are being done to test the nature of the transformation by measuring the effect of replacing hydrogen by deuterium on the transformation pressure, and similar experiments are being done on the transformation of the low-density amorph to the high-density phase.

### III. STRUCTURE OF THE AMORPHOUS PHASES BY RAMAN SPECTROSCOPY

Diffraction methods are, of course, the most general for determining the structure of solids. However, the most detailed information about the structure of hydrogen-bonded phases like ice can probably be obtained from the Raman spectrum of the uncoupled O-H and O-D oscillators. The frequencies of these oscillators are particularly sensitive to the O--O distance, and are much less sensitive to other structural factors, such as the linearity of the O-D--O bonds, and the scattering intensity does not change greatly with O--O distance. Consequently, the Raman spectrum of the uncoupled O-H and O-D oscillators has been used to determine the distribution of hydrogen-bonded O--O distances in the high-density amorph and the phases made by heating it controllably [unpublished].

In order to measure the Raman spectrum, clear samples of the high-density amorph embedded in small copper channels were made in a piston-cylinder apparatus at 77 K and 16 kbar. Excess ice was cleared away and the surfaces of the ice were polished. The sample was then mounted on the tail of a Displex closed-cycle refrigerator without its temperature rising above 77 K. The Raman spectrum at ~12 K was recorded of the sample as recovered and after heating it in the Displex to 80, 90, . . . , K for 5 min and cooling it to 12 K. Representative spectra so obtained are plotted in Fig. 2. The cooling from 77 to 12 K has only a small effect on the frequencies because of the third law.

The uncoupled O-H and O-D frequencies were converted to hydrogen-bonded O--O distances by using a relation between the peak frequencies of the uncoupled O-H band and the O--O distance that was obtained from the infrared spectrum of ice VII at 295 K in the range 20-185 kbar [4]. This relation was scaled to the uncoupled O-D frequency, and both were scaled to low temperature to make them agree with the peak Raman frequencies of the uncoupled O-H and O-D bands of ice II and IX. The final equations are

$$\nu_{\text{OH}}/\text{cm}^{-1} = 3707.47 - 3409.4 \exp[-R/(1.12 \text{ \AA})] - 683\,490 \exp[-(R/0.896 \text{ \AA})^2] \quad (1)$$

and

$$\nu_{\text{OD}}/\text{cm}^{-1} = 2786.16 - 1015.2 \exp[-R/(1.190 \text{ \AA})] - 353\,120 \exp[-(R/0.955 \text{ \AA})^2]. \quad (2)$$

The distribution of O--O distances in the high-density amorph is reproduced in the first column of Fig. 3, of the low-density amorph in the second, and of ice Ic and Ih in the third. The distribution in the high-density amorph is very broad, the most probable distance being 2.83 Å and the distances at half the peak height being 2.94 and 2.76 Å, and the distribution narrows significantly when the amorph is annealed. Between 110 and 120 K, the ice transforms to the low-density amorph and the distribution of distances narrows, and it narrows further when the sample is heated to 150 K and transforms to ice Ic.

The relation between the high-density amorph at 77 K and the liquid can be explored by comparing the uncoupled O-H and O-D Raman frequencies of the liquid under pressure [5] and of the high-density amorph that has been scaled to 10 kbar. The O--O distance of the amorph at zero pressure was scaled to 10 kbar by the cube root of the ratio of densities, and the frequencies were calculated from Eq. (1) and (2). They are 3236 and 2392 cm<sup>-1</sup> respectively, which are lower than the frequencies 3380 and 2490 cm<sup>-1</sup> respectively in the liquid at 298 K and 10 kbar [5] by 144 and 98 cm<sup>-1</sup>. The difference is of the magnitude expected for the difference of temperature, and so the high-density amorph and the liquid appear to be closely related.

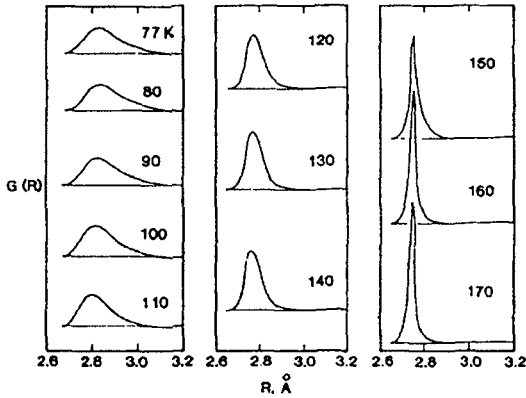


Fig. 3. Distribution of hydrogen-bonded O-O distances in high-density amorphous ice at ~12 K. The samples were recovered at 77 K and were heated in succession to the temperatures attached to the curves and held there for 5 min.

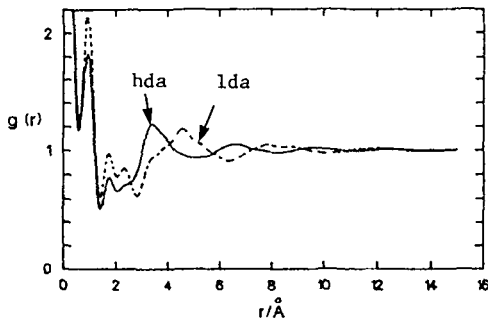


Fig. 4. Neutron-weighted radial distribution function of high-density and low density amorphous ice, which are labelled hda and lda respectively, at 17 K.

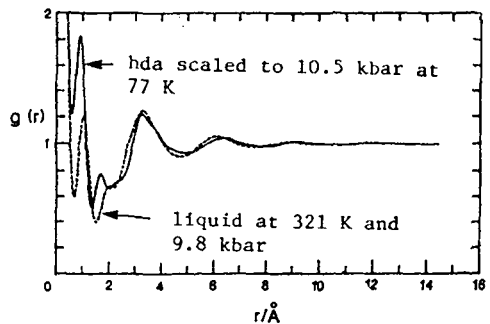


Fig. 5. Neutron-weighted radial distribution function of high-density amorphous ice recorded at zero pressure, as scaled approximately to 10 kbar by dividing all distances by the cube root of the ratio of the densities at 10 kbar and zero pressure. The curve, which is the solid line, is compared with the pair correlation function of D<sub>2</sub>O water at 321 K and 9.8 kbar.

IV. STRUCTURE OF THE AMORPHOUS PHASES BY NEUTRON DIFFRACTION

The neutron-diffraction pattern in the range 0-12 Å<sup>-1</sup> of a sample that was 70 mm in diameter and 1.5 mm thick and was held at 17 K in a Displex closed-cycle refrigerator was measured with the N5 spectrometer at the NRU Reactor in Chalk River [unpublished]. It was adjusted to allow for absorption, multiple scattering, and inelastic scattering, and was multiplied by a constant factor to convert the scattering at large momentum transfer to the value predicted for randomly distributed water molecules, which is 0.334. The resulting curve, which is the structure factor, was extrapolated smoothly through zero at zero momentum transfer and was Fourier transformed in the usual way to obtain the neutron-weighted radial distribution function. The distribution function of the high-density amorph, which is drawn as the solid line, is compared in Fig. 4 with that of the low-density amorph, which is drawn as the dashed line. The density of the low-density amorph is 0.94 g cm<sup>-3</sup> and it was made by heating the high-density amorph to 130 K [6]. There is little resemblance between them, except at low radii. It is, of course, not surprising because the densities differ by 25%. The x-ray diffraction patterns of the two phases are also quite different [7].

It is more appropriate to compare the radial distribution functions of the liquid at 9.8 kbar and 321 K [8] with the radial distribution function of the high-density amorph at 17 K that has been scaled to the density at 10 kbar since the high-density amorph was prepared at 10 kbar. The scaling was done by dividing the density by the cube root of the ratio of densities at 10 and 0 kbar and the two curves are plotted in Fig. 5. The curves are remarkably similar, except at low radii where the scaling is invalid, and they support the supposition that the high-density amorph is similar to what we would expect to obtain if we could rapidly quench the liquid to the glass at 10 kbar.

In summary, the high-density amorph appears to be closely related in several ways to the (so far) hypothetical solid that would be obtained by quenching the liquid at 10 kbar fast enough.

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#### COMMENTS

S. KIRBY

You might expect the O-H...O bond angles to be more non-linear in the glassy high density amorphous phase compared to the liquid. Could this account for the small difference in Raman frequencies for those two phases via the well-established effect of O-H...O bond angle on the hydrogen-bond length versus O-H frequency relation ? (one might expect the glass to have more bent O-H...O bond angles than the liquid).

Answer :

We have neglected the effect of bending the hydrogen bond on the frequency because it is not well known and because it is even in the bending and so may be a second order effect. Small differences in frequency may be due to this effect, but we do not know the structure of the high-density amorph well enough to tell.

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T. MATSUO

The DTA peak is exothermic on the heating run, which means that the high density-low density change is irreversible. Is it possible to run the DTA reversibly between the two amorphous states ?

Answer :

There is no evidence that the transformation from high-density to low-density amorph goes reversibly. The reason may be that the surface of the high-density amorph does not become unstable at the surface when the pressure is reduced and so there may be no mechanism at such low temperatures.

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J.M. WARMAN

Could you comment on the similarities and/or differences between the high density or low density forms of ice and the structure of the glassy aqueous media formed on cooling of high concentration salt solutions (e.g. perchlorates).

Answer :

I regret I know little about such glassy materials. The water near the ions may be compressed by the electric field of the ions, and so may transform to a high-density glass. The density of the glass may tell about this.

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P. BOUTRON

What are the densities of the high and low densities forms of amorphous ice ?

Answer :

The density of the low-density amorphous ice is about  $0.94 \text{ g cm}^{-3}$  at zero pressure and that of the high density amorph is  $1.17 \text{ g cm}^{-3}$ . The high density amorph at 10 kbar has a density of  $1.31 \text{ g cm}^{-3}$ .

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W.F. KUHS

From the different ways of preparation one could suspect that your high-density amorphous ice is not identical to the high-density amorphous ice produced (irreproducibly ?) by Rice et al . Can any thing be said about the similarities and differences of the two phases ?

Answer :

The high-density amorphous ice referred to by Dr. Kuhs was briefly reported by Venkatesh, Rice, and Narten in 1974<sup>1</sup>, was reported more fully by the same authors in 1976<sup>2</sup>, and was withdrawn in the abstract of Ref. 3.

<sup>1</sup> G.C. Venkatesh, S.A. Rice and A.H. Narten, Science 186, 927-928 (1974).

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