X-Ray Study of High-Density Amorphous Water

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X-ray diffraction measurements were performed at atmospheric pressure on a high-density form of amorphous ice obtained by pressurization of crystalline ice Ih at 77 K, up to 2 GPa. The low–momentum-transfer region of the determined structure factor is quite different from that corresponding to the low-density form of amorphous ice. However, the nearest-neighbor distance and coordination number are almost unchanged. The high density of this form of amorphous ice is explained by the strong distortion of the O-O-O angles from the ideal tetrahedral value.

In spite of the intensive study of liquids and non-crystalline solids, our knowledge about the structure of these materials under pressure is still incomplete. Recently, a new method to obtain a high-pressure form of amorphous water has been successfully applied[1]: When compressed at 77 K, ice Ih transforms to a non-crystalline solid above 1 GPa. The transformation is irreversible: When the pressure is released, the sample is only elastically expanded. It is then possible to study this form of amorphous ice at atmospheric pressure.

In this Letter, the O-O correlations measured by x-ray diffraction are reported. They were obtained with heavy water, so that the present results can be compared with the neutron diffraction data, when such data become available.

The sample was prepared according to the procedure previously described by Mishima, Calvert, and Whalley.[1] About 1.5 cm^3 of heavy water was poured into a piston-cylinder apparatus (inner diameter 10 mm) and cooled to 77 K. A force was applied to the piston by means of a hydraulic press and the piston displacement was recorded during the application of the pressure. The high-density form appeared in the 1.0- to 1.3-GPa range, as measured by an electrical pressure transducer located in the oil circuit of the press. Thus it seems that deuteration has a negligible effect on the pressure of such transformation. The error due to friction was assumed to be negligible. On removal of the pressure the transition was not reversible. A subsequent compression of the sample did not show any effect. A special device was used to extract the plug from the high-pressure cell and to fill the x-ray diffraction sample

holder with the high-density amorphous ice at 77 K, i.e., in liquid nitrogen.

The sample holder was a 8-mm-diam, 15-mm-high cylinder of aluminized Mylar, 10 μm thick, wrapped inside a cylindrical copper block provided with two windows for the x-ray path. This sample holder could be automatically clamped in liquid nitrogen at the bottom of a cryostat after being filled with the sample. The cryostat was equipped with two plane Be windows to allow passage of the incident and diffracted x-ray beams and to maintain a uniform temperature of the sample. The temperature was measured by a copper-Constantan thermocouple located inside the Mylar container. After attachment of the sample holder within the previously cooled cryostat, the sample was maintained in vacuum.

The x-ray data were collected by use of a standard diffractometer operating with a molybdenum tube ($\lambda = 0.7093$ Å) in a step-scanning mode with steps equal to $0.1°$ (2θ). Monochromatization was obtained with a bent quartz monochromator in the incident beam. The experiments were performed in the transmission mode. Because of the dimensions of the copper block containing the sample holder, the angular range was limited to $62°$ (2θ) so that the momentum transfer $q = 4\pi \sin\theta/\lambda$ extended from 0.3 to 9.0 Å^{-1}. Several samples were prepared but the x-ray diffraction measurements revealed spurious Bragg peaks, in particular around 2.2 Å^{-1}. These were attributed to the undesirable contamination of the sample by the formation of high-pressure crystalline forms of ice. After different attempts, we succeeded in obtaining a sample completely free from such contamination, that

is, free of any crystalline material.

The duration of the data collection was three weeks, during which time all the measurements were done, all at liquid-nitrogen temperature, 77 K. The following forms of the samples were measured successively: (a) high-density amorphous water prepared as described above; (b) low-density amorphous water formed after heating of the sample to 140 K and subsequent cooling to 77 K; (c) crystalline ice Ic formed after heating to 190 K and cooling to 77 K; (d) crystalline ice Ih formed after heating to 250 K and cooling to 77 K.

Figure 1 shows the scattered intensity of x-rays by each of these forms. The upper curve [Fig. 1(e)] is the scattered intensity by the sample in the liquid state at ~ 298 K at 1 atm, obtained after release of the vacuum. Figure 1 clearly indicates the following: (i) On pressurization at 77 K of hexagonal ice (Ih), an amorphous phase is formed as observed by Mishima, Calvert, and Whalley.[1] (ii) On heating, this amorphous

solid transforms to another form, the transformation being achieved when the temperature reaches 140 K (Mishima, Calvert, and Whalley[1]). (iii) The second amorphous solid transforms into cubic ice (Ic) on heating to 190 K, as deduced from the indexing of the Bragg peaks. (iv) Finally, the metastable Ic phase transforms to the usual hexagonal phase (Ih) on further heating. Note that the (10.0), (00.2), and (10.1) reflections are clearly resolved in spite of the large size of the sample.

The measured intensities were corrected for the sample-holder absorption and scattering, for polarization and absorption in the sample, and for incoherent scattering and normalized to derive the coherent structure factor $S(q)$. The results are shown in Fig. 2 for the polymorphic amorphous forms of water. From these calculations one can first conclude that the structure factor of the low-density amorphous solid water obtained after the transformation of the high-pressure form is similar to that reported for amorphous water prepared by vapor deposition on substrates at 77 K.[2]

A comparison of the two structure factors indicates the following: (i) There is a significant difference in both the shapes and positions of the two main peaks of $S(q)$ in the low-q range (located at 2.10 and 3.07 Å^{-1} for the high-density form and at 1.63 and 3.05 Å^{-1} for the low-density form). (ii) On the contrary, the structure factors of both forms of amorphous ice are similar in the high-q range (typically above 6 Å^{-1}), suggesting the same near-neighbor environment in the two phases.

The Fourier inversion of the structure factor gives the pair-correlation function $g(r)$ for the molecular
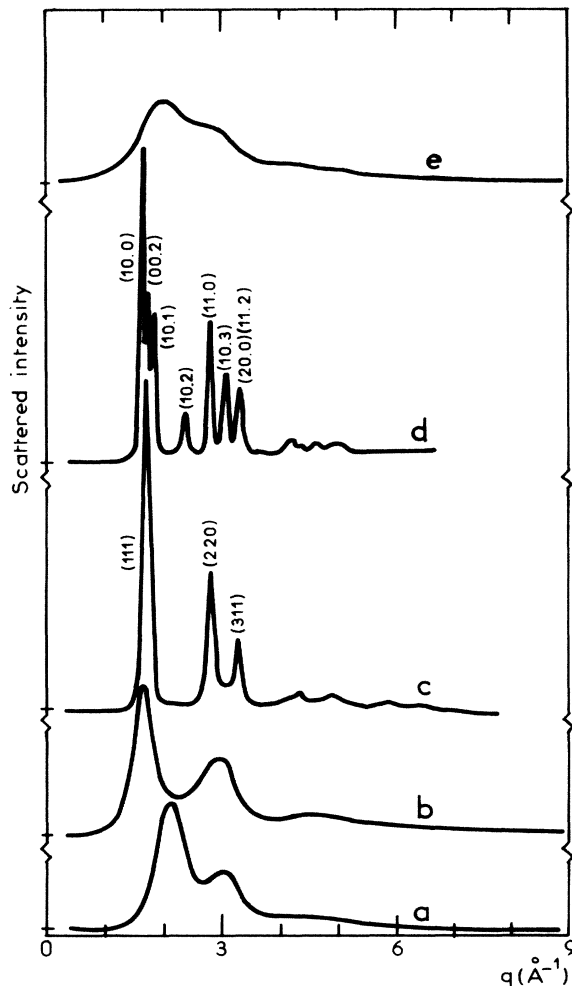

FIG. 1. X-ray scattered intensity by water: (a) high-density amorphous; (b) low-density amorphous; (c) cubic ice; (d) hexagonal ice; and (e) liquid.
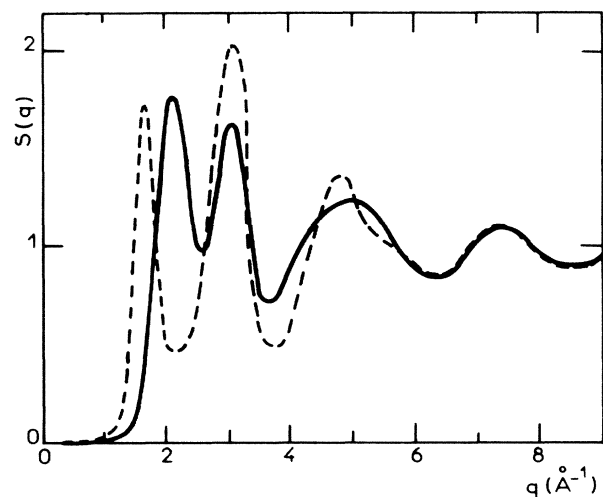

FIG. 2. Structure factor of the two forms of amorphous ice at 77 K: solid line, high-density form; dashed line, low-density form.

centers:

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

The upper limit of 9 $\mathring{A}^{-1}$ in the structure-factor data in Fig. 2 produces spurious ripples in the low-r range because of the truncation in the evaluation of the Fourier transform. In order to detect the importance of such effects, the calculations were carried out with and without a weighting by the Hanning function.

Figure 3 displays the pair-correlation functions of the two amorphous forms of ice, as obtained before the truncation correction [Fig. 3(a)] and after such a correction [Fig. 3(b)]. As expected, in this last case, the resolution is ineluctably affected. However, the comparison of the two figures shows that the truncation effect is not too severe beyond 2 $\mathring{A}$ and further discussion will be based on Fig. 3(a).

The first-nearest neighbors are located at the same distance, 2.8 $\mathring{A}$, and the coordination number, obtained from the radial distribution function $D(r)$ = $4\pi r^2 \rho g(r)$, is ~ 4. This indicates that, at the level of the first neighbors, the two forms of amorphous ice
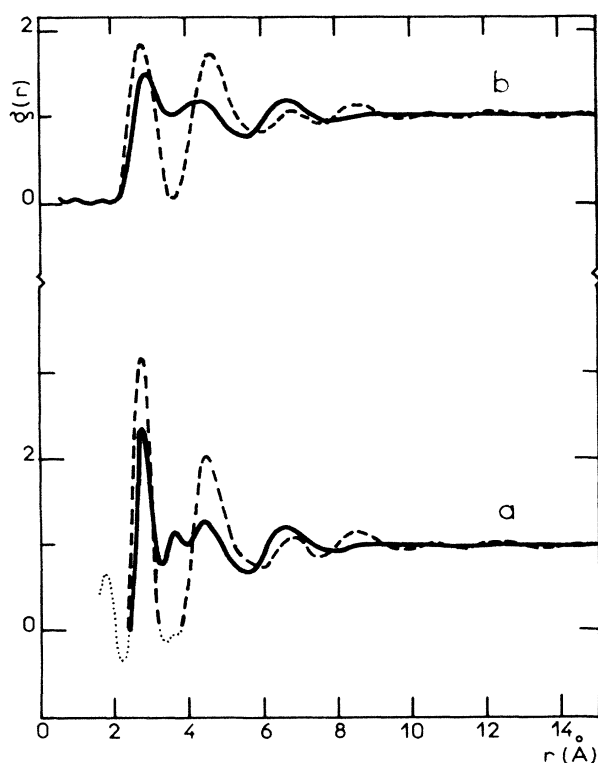

FIG. 3. Pair-correlation function of the molecular centers for the two forms of amorphous ice: solid line, high-density form; dashed line, low-density form. (a) Before correction of the truncation effects due to the limitation at 9 $\mathring{A}^{-1}$ of the scattering data. (b) After correction by a smoothing function. The main differences occur in the region following the first-nearest neighbors.

appear to be analogous and exhibit the characteristic tetrahedral coordinations. The small difference in the height of the first $g(r)$ peak is probably not significant.

The main differences between the two pair-correlation functions appear at the level of the second- and third-neighbors. For the low-density form, the second-nearest neighbors are clearly separated from the first ones and the two peaks in $g(r)$ are perfectly resolved and separated by a deep well. On the contrary, for the high-density form, the second-neighbor peak is split into two peaks and the well separating them from the first peak is less pronounced. Another difference lies in the rapid loss of order at high r in the high-density solid water.

It is interesting to mention that the 3.5-3.6-$\mathring{A}$ peak in $g(r)$ is analogous to the peak observed in the amorphous form of ice which was obtained by slow deposition of water vapor on a substrate cooled at 10 K.[2] The existence of such a shoulder in liquid water has often been discussed in the literature.

We interpret the observed pair-correlation function in the high-density form of amorphous ice in terms of the bending of hydrogen bonds. This corresponds to a disortion of the O-O-O angles out of the ideal tetrahedral value of 109°. It is worth emphasizing that this structure is completely different from that observed in supercooled water.[3,4] With decreasing temperature, the O-O-O angles in supercooled liquid water open towards the ideal tetrahedral angle. Therefore, it would seem that the high-density amorphous form may not have the same structure as the glassy form obtained by the supercooling of liquid water.

The importance of the angular correlations in the structure of water has been emphasized in previous studies of supercooled water.[3,4] Neutron scattering studies will probably give better support to our interpretation because of their sensitivity to the O-D and D-D pair-correlation functions.

Finally, it is interesting to mention that the high-density form of amorphous ice that we prepared from ice Ih can be obtained by starting from the low-density amorphous form.[1] This polymorphism of the amorphous forms can be compared to the analogous situation observed in silica.[5] The analogy between the structure and the thermodynamic properties of water and vitreous silica has been already pointed out.[6,7] In both materials, the occurrence of the tetrahedral symmetry is at the origin of short-lived ordered patches and enhanced density fluctuations.[8] The application of pressure does, in general, reduce this symmetry and suppress most of the thermodynamic anomalies. It is interesting to note, in this context, that the displacement that we observed in the position of the first peak of the structure factor is identical to that observed in water under pressure.[9,10]

X-ray diffraction and neutron measurements in a

larger q range are still necessary to obtain the structure of the high-density form of amorphous ice more precisely. This work is in progress.

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