Structure of High-Density Amorphous Ice under Pressure

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We report *in situ* neutron diffraction studies of high-density amorphous ice (HDA) at 100 K at pressures up to 2.2 GPa. We find that the compression is achieved by a strong contraction ($\sim 20\%$) of the second neighbor coordination shell, so that at 2.2 GPa it closely approaches the first coordination shell, which itself remains intact in both structure and size. The hydrogen bond orientations suggest an absence of hydrogen bonding between first and second shells and that HDA has increasingly interpenetrating hydrogen bond networks under pressure.

DOI: 10.1103/PhysRevLett.89.285502

When ordinary ice Ih is compressed to 1.5 GPa at 77 K it transforms to high-density amorphous ice (HDA) [1] which remains metastable to structural transitions at ambient pressure. Although the ice Ih to HDA transition has been widely studied there is still much controversy about the form of ice that is produced. One line of argument suggests that HDA and its counterpart, low-density amorphous ice (LDA), to which HDA transforms when heated to ~ 115 K at ambient pressure, form the amorphous analog of a two-phase liquid system below a liquidliquid critical point at about 220 K [2]. Other lattice dynamics work [3] has been taken to suggest that the ice Ih to HDA transition is in fact a mechanical collapse of the ice Ih structure to an amorphous form that may be different in structure from the liquid, although molecular dynamics (MD) studies [4] suggest the structures of the liquid and amorphous states are continuous. In a recent study, Finney et al. [5] measured the site-site radial distribution functions for LDA and HDA using neutron diffraction and hydrogen isotope substitution, and estimated the spatial distribution functions in both systems. They showed that the structure of liquid water is indeed quite analogous to HDA and noted the presence of a socalled nonbonded "interstitial" molecule close to the first coordination shell of water molecules in both HDA and liquid water. This molecule is not present in LDA or in ice Ih but is reminiscent of the four nonbonded first neighbor molecules found in ice VII [6]. Another study of water structure under pressure [7,8] shows that the second coordination shell compresses as the pressure is raised, while the first shell remains largely unchanged. Given the apparent similarity between liquid water and HDA the question arises as to what exactly is the nature of HDA at different pressures?

PACS numbers: 62.50.+p, 61.12.-q, 61.25.-f, 61.43.Er

In fact all the structural work on HDA to date is on the "recovered" metastable form, obtained after releasing the pressure back to ambient. We present here the first *in situ* diffraction study of HDA, extending over the entire range of its existence, up to ~ 2.5 GPa. Our studies are aimed at providing detailed insight into the structural changes of HDA under variable density. Such measurements become possible due to progress in high-pressure methods using the Paris-Edinburgh cell [9], as well as data analysis techniques for disordered systems [8]. We show that it is indeed possible to obtain detailed and reliable structural data from a ~ 80 mm³ sample of HDA under pressure in the 1–2 GPa range.

All experiments were performed on the PEARL station of the ISIS neutron facility at the Rutherford Appleton Laboratory (U.K.). HDA was produced by loading water (D_2O) into the Paris-Edinburgh cell equipped with sintered diamond (SD) anvils, cooling to 85 K to give ice Ih, followed by a slow compression at a rate of 1 GPa/h. After data collection at 2.2, 0.7, and 0 GPa for typically 10 h each, the sample was carefully removed from the cell, and the gasket and anvils reassembled in exactly the same way to measure the background under strictly identical conditions, at the same temperature. The signal determined in this way was subtracted from the overall signal (b/s ratio typically 10%). The diffraction patterns were then corrected for the wavelength-dependent attenuation due to the anvil material as done in standard measurements using this high-pressure cell [10]. The patterns obtained are shown in Fig. 1, which also compares our 0 GPa spectrum with the best available atmospheric-pressure S(Q) data [inset (a)] [11]. The data are free from any contaminant scattering from the pressurecell materials and, although the small sample volume limits the statistical precision, it can be seen that there is excellent agreement with Ref. [11]. These patterns indicate significant structural modifications: at 2.2 GPa, the main peak has shifted to lower *d* spacings by ~ 0.3 Å and reduced by $\sim 30\%$ in width.

It is not possible to determine the pressure directly in our measurements. The pressure values quoted here were determined in separate runs using HDA samples mixed with nontransformed ice Ih or ice VII (to which HDA transforms beyond ~2.5 GPa), by calibrating the position of the strongest diffraction feature of HDA at ~2.6–3.0 Å using the known equations of state of these crystalline ice phases. These values are also consistent with other measurements where pure HDA samples were warmed isobarically to transform to various ice phases, for which the pressure can be determined accurately. The density of HDA, the relevant parameter for the data analysis described below, was then determined from published p-V measurements to 1 GPa [1,12], extrapolated to 2.2 GPa. The estimated errors in pressure are ± 0.1 GPa at 0.7 GPa



FIG. 1 (color online). Principal peak in neutron diffraction patterns from HDA at 0 and 2.2 GPa (main figure). Inset (a) compares the complete 0 GPa data (upper plot) with published ambient pressure S(Q) data [11] plotted as a function of $Q = 2\pi/d$. Inset (b) shows the phase diagram of water, including the domain of existence of HDA. The broad line shows schematically the recrystallization temperature and dashed lines are extrapolated phase boundaries. The arrows show the *P*-*T* paths followed in the recrystallization experiments mentioned in the text.

and ± 0.2 GPa at 2.2 GPa. This relates to errors in density of $\pm 2\%$ at most (less than 1 molecule/nm³).

Our data were analyzed by a Monte Carlo refinement technique (empirical potential structure refinement [7,8], EPSR), a method which was successfully applied previously for the analysis of low and high-density water [7,8] as well as LDA and HDA [5]. EPSR is not a standard reverse Monte Carlo algorithm. The refinement procedure makes use of realistic intra- and intermolecular potentials to constrain the geometry of the water molecules while simultaneously making the best possible fit with the measured structure factor. Compared to simple Fourier transform methods, EPSR has the advantage of providing all three partial correlation functions $g_{\alpha\beta}(r)$ and the three-dimensional distribution around a given D₂O molecule. EPSR is also free from truncation artifacts that are inherent in Fourier transformation methods.

The results of the refined $g_{\alpha\beta}(r)$ are shown in Fig. 2. Out to the first peak in $g_{OO}(r)$, the features are all those expected for tetrahedral H bonding, with an $O \cdots O$



FIG. 2 (color online). Site-site radial distribution functions $g_{\alpha\beta}(r)$ of HDA at 0, 0.7, and 2.2 GPa, and $g_{OO}(r)$ data for water at 0 and 0.4 GPa at 268 K [8]. The first peaks in $g_{OD}(r)$ (at ~1.8 Å) and $g_{DD}(r)$ (at ~2.2 Å) are, respectively, the D···O hydrogen bond length and the intermolecular D-D distance. The strong intramolecular contributions to $g_{OD}(r)$ and $g_{DD}(r)$ at 1.0 and 1.5 Å have been subtracted for clarity.

distance of \sim 2.8 Å, and these features show no significant change with pressure. However, the second peak in $g_{OO}(r)$ at ambient pressure is centered at 3.7 Å rather than the 4.5 Å expected for the second-neighbor tetrahedral bonding seen in LDA, ice Ih, and low-density water [5]; and this peak moves rapidly to even lower r with pressure so that by 2.2 GPa it is a shoulder on the first peak at 2.8 Å. The third and fourth peaks also move strongly to lower rwith pressure. Integrations of $g_{OO}(r)$ reveal that there are about 12 molecules over the range 3.1-4.6 Å at ambient pressure, as expected for the second coordination shell. As this second peak moves to shorter r with increasing pressure, fewer molecules are associated with it. At 2.2 GPa, integration of $g_{OO}(r)$ to 3.5 Å gives a coordination number of 9.0 (2) suggesting that, in addition to the four molecules of the unchanged first shell at 2.8 A, a further \sim 5 molecules are associated with the main part of the shoulder that remains from the initial second peak. Integration of $g_{00}(r)$ from 3.5 to 4.6 Å reveals that there are another ~ 8 molecules in this region.

The corresponding spatial distribution functions (SDFs) of the oxygen density plotted in Fig. 3 show the expected tetrahedral arrangement for the first coordination shell, and that the form and radius of this shell are pressure independent as expected. The second shell SDF forms another approximately tetrahedral arrangement, inverted with respect to that of the first shell. Though the spatial arrangement of this tetrahedron is unaffected by pressure, its radius shrinks rapidly, as $g_{OO}(r)$ shows, and approaches the radius of the first shell at 2.2 GPa. Under pressure, the central molecule thus shows a trend towards an increased coordination that has a quasi-body-centered cubic arrangement similar to that of ices VII and VIII [6].

The question arises as to how the first and second shells are connected, if they are, given the short and very pressure-dependent second shell distance. The insets in Fig. 3 show distribution functions for the orientations of the D_2O dipoles in these two shells at the locations indicated. As can be seen, the dipoles in the first shell are preferentially directed radially over a relatively small angular range, and thus generally cannot donate H bonds towards the second shell molecules, which are at positions approximately in a plane normal to the radial direction concerned. The dipoles in the second shell (Fig. 3, inset) are directed over a wide range of tangential directions. Although some of these directions do direct H atoms towards first neighbor molecules the majority of orientations do not. And in any case the distance of more than 3.5 A from second to first neighbor molecules is too long to be an H bond. Thus, the majority of the second shell molecules cannot donate H bonds either towards the original molecule or towards the first shell molecules. We note that Finney et al. [5] also concluded that the fifth interstitial molecule found in their analysis of ambient pressure data was not bonded to the central molecule.



FIG. 3 (color). The main plots show the spatial distribution functions (SDFs) of the oxygen atoms. The upper plots were obtained from data collected at 0 GPa and show (left) the density in the range 2.0-3.1 Å (the first coordination shell) and (right) from 2.0-4.8 Å (the first and second coordination shells). The middle plots, from data collected at 0.7 GPa, show (left) the density in the range 2.0-3.1 Å and (right) from 2.0-4.6 Å. The lower plots, from data collected at 2.2 GPa, show (left) the density in the range 2.0-3.0 Å and (right) from 2.0-4.3 Å. The insets show the distribution of dipole orientations for water molecules at the arrowed positions in the SDFs. The levels of all isosurfaces have been set to enclose 40% of the molecules within the specified ranges.

This hydrogen bonding configuration suggests that HDA has a radically different structure from LDA. The SDF's and $g_{OO}(r)$ of LDA reveal a tetrahedral H-bond network at least out to the second shell — as indicated by the peak at 4.5 Å in Fig. 3 of Ref. [5]. The lack of H-bond connection between first and second shells in HDA suggests that, out to two H-bond contacts from the original molecule, HDA under pressure shows the characteristics of having interpenetrating H-bonded networks as found in ices VI, VII, and VIII. (It is interesting to note that the pressure of the transition from ice *Ih* to HDA is close to

that at which ice VI – the first ice to have interpenetrating networks — becomes stable.)

A key point to emerge is that the H-bond topology of HDA is present even for samples recovered to ambient pressure, though the coordination undergoes large changes with pressure. As we have seen, HDA is essentially fourfold coordinated at ambient pressure, with a broad shell of some 12 molecules starting at a slightly higher r, and with increasing pressure it trends towards eightfold coordination with four H-bonded neighbors and four nonbonded neighbors in a configuration which is very like that found in ices VII and VIII. This is consistent with Finney et al.'s observation of a fifth, interstitial, molecule at ambient pressure [5]. But their conclusion is based on integration out to only 3.3 Å, and our results reveal that this fifth molecule and the associated patches in the SDFs in Ref. [5] are simply the short r part of the broad second shell.

Comparing our $g_{00}(r)$ rdfs with those of water obtained by Soper and Ricci [8] (Fig. 2), we conclude that HDA at ~ 0.7 GPa resembles liquid water at 0.4 GPa and that liquid water at 0 GPa would resemble HDA at somewhat negative pressures (to adjust for the difference in density). This may well signify a tendency towards interpenetrating networks in water, and such a conclusion is supported by molecular dynamics studies of water up to 10 GPa [13,14]. These provide microscopic evidence of a liquid structure very like that of ice VII at the highest pressures. The strong resemblance of $g_{\alpha\beta}(r)$ of HDA and liquid water under pressure may also rationalize the recrystallization behavior of the two systems. In extensive in situ studies [15,16], we have shown that HDA crystallizes into the same phases as would be formed on cooling liquid water at approximately the same density, rather than into the equilibrium forms at low temperatue. This behavior has also been reported in studies of recovered samples [17,18].

It is interesting to note that dipole orientations also reveal there is a tendency for the dipoles of the secondneighbor molecules to be oriented parallel to that of the original molecule. This is markedly different from ice VIII where the nearest nonbond neighbors have antiparallel dipole directions. However, it should be noted that HDA is found only at temperatures below those at which dipole rotation is activated and thus may have a nonequilibrium orientation distribution. It may be that this situation persists on crystallization and hence that ice VII produced from HDA at low temperatures differs from thermodynamically stable ice VII at room temperature in its local orientational correlations.

The difference in network topology between HDA and LDA suggests the transition between the two forms is not continuous, and the interpretation of other measurements — for example, spectroscopic studies — needs to incorporate the presence of network interpretation

and short nonbond $O \cdots O$ contacts. Similarly, the strong coordination change with pressure means that the structure of HDA under the conditions at which it forms is significantly different from that obtained at ambient pressure. Conclusions on the nature of the transition to HDA based on data obtained from recovered samples need to incorporate these strong structural changes.

We acknowledge very helpful discussions of our results and conclusions with D. D. Klug and M. Saitta. Our work (J. S. L., R. J. N., M. G.) is funded by a research grant from EPSRC, and supported by CCLRC through access to beamtime and other resources.

Note added.—The work of Finney et al. on LDA and HDA [5] has now been extended to a similar study of very high density amorphous ice (VHDA) [19], an apparently distinct structural form [20]. A considerable difference in structure is found between VHDA and HDA compared at ambient pressure [19]. However, the density, radial distribution functions, and SDFs obtained for VHDA at ambient pressure are all essentially the *same* in their key features as those we find for HDA at ~0.7 GPa. It thus seems necessary to seek the principal difference between VHDA and HDA elsewhere.

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