Neutron-diffraction study of phase transitions of high-pressure metastable ice VIII

A. M. Balagurov, O. I. Barkalov, A. I. Kolesnikov, G. M. Mironova, E. G. Ponyatovskiĭ, V. V. Sinitsyn, and V. K. Fedotov
Institute of Solid State Physics, Academy of Sciences of the USSR

(Submitted 30 October 1990; resubmitted 29 November 1990)
Pis'ma Zh. Eksp. Teor. Fiz. **53**, No. 1, 30–33 (10 January 1991)

The transformation of a quenched phase of high-pressure ice as a result of heating it from 94 K to 290 K has been studied by means of neutron-diffraction in real time. The following sequence of transitions has been established: ice VIII, amorphous high- and low-pressure phases, cubic ice, hexagonal ice. The formation of high-density amorphous ice from phase VIII has been observed for the first time.

It was shown in Refs. 1 and 2 that in addition to the crystal modifications, ice produces two amorphous phases: with low and high densities which we designate below as *hda* and *lda*, respectively (high and low density amorphous phases). To obtain ice *hda*, we cooled a hexagonal ice I*h* to liquid-nitrogen temperature and then compressed it to a pressure of ~1 GPa. After removing the pressure, we observed the following sequence of transformations in the ice as a result of heating:[3]

$$hda \xrightarrow{140\mathrm{K}} lda \xrightarrow{190\mathrm{K}} \mathrm{I}c \xrightarrow{250\mathrm{K}} \mathrm{I}h, \qquad (1)$$

where I*c* is the cubic phase of the ice.

If the ice *hda* is further compressed, it will undergo, at a pressure of ~4 GPa, a transition to phase VII or phase VIII,[4] depending on the temperature at which the compression occurs.

Another way of obtaining amorphous ice was found: specifically from a quenched high-pressure phase, phase VIII.[5] Heating produced the following transitions:

$$\text{ice VIII} \longrightarrow lda \longrightarrow \text{I}c \longrightarrow \text{I}h. \qquad (2)$$

It was assumed in Ref. 5 that an amorphous low-density ice is formed from an amorphous high-density ice, although the ice *hda* could not be observed experimentally. On the basis of calorimetric experiments it was assumed[6] that ice *hda* should apparently exist at temperatures in the range 127–136 K.

Using a neutron-diffraction method, we have experimentally studied, in real time,[7] the transformation of metastable high-pressure ice as a result of heating it, in order to observe the transition ice VIII→*hda*.

The sample (99% D_2O) weighing 0.3 g was compressed at room temperature in a "shaped anvil–lens" chamber[8] to a pressure of 2.6 ± 0.3 GPa and held under those conditions for 1 h in order to establish equilibrium. After this procedure, the chamber was cooled with liquid nitrogen to ~ 100 K and at this temperature the pressure was lowered to the atmospheric pressure. All subsequent procedures involving the sample before the beginning of the measurements were carried out at liquid-nitrogen temperature.

The neutron-diffraction experiment was carried out with use of a time-of-flight DN-2 diffractometer in an IBR-2 reactor in Dubna.[9] The neutrons were detected by detectors placed at angles $2\theta \simeq 90°$ and 150°. The sample in a Teflon cell was immersed in a helium cryostat with aluminum ports. The sample was heated at a rate of ~ 1 deg/min, at temperatures in the range 94–290 K, with an exposure time of 5 min for a single neutron-diffraction pattern.

Figure 1 shows the sequence of neutron-diffraction spectra measured during the

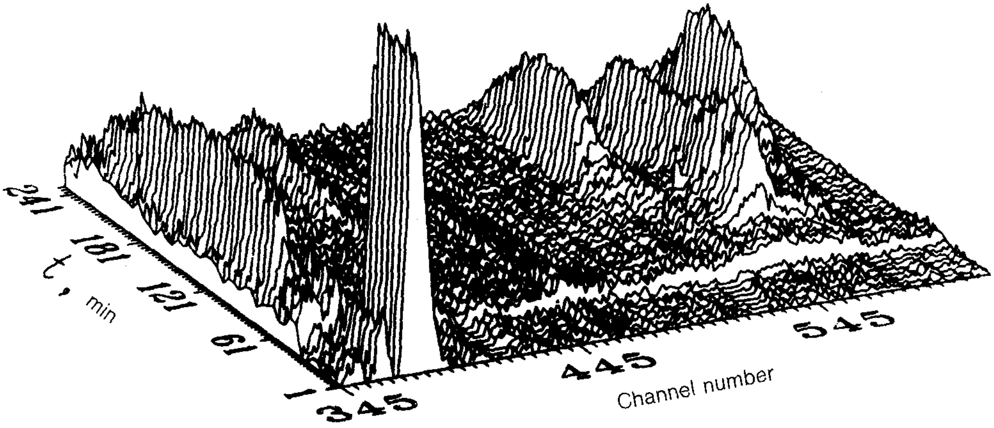

FIG. 1. Neutron-diffraction patterns of ice in the temperature interval 94–290 K. The heating was carried out at $\Delta T/\Delta t \simeq 1$ deg/min. $T = 94$ K corresponds to zero time.

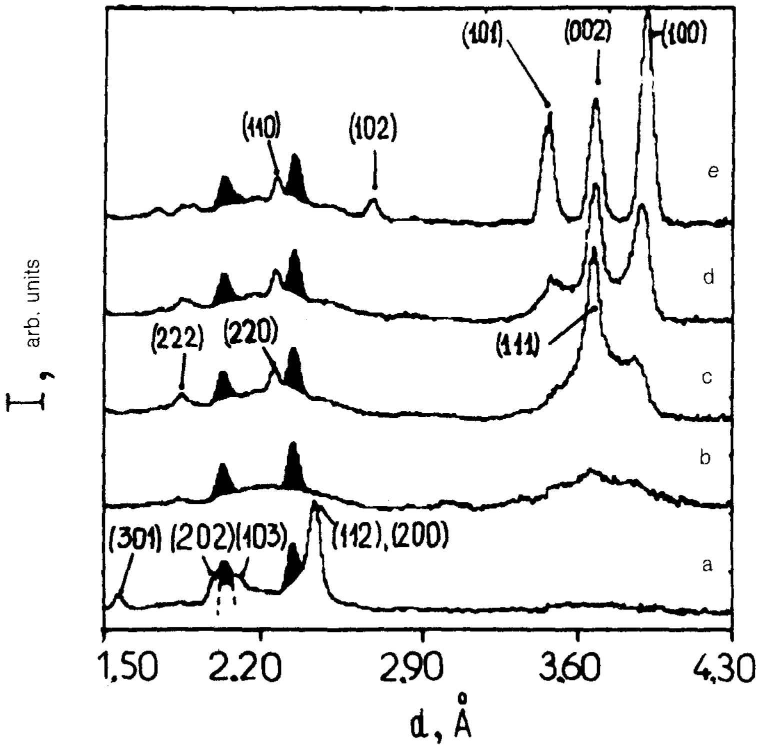

FIG. 2. Neutron-diffraction patterns of various phases of ice. (a) High-pressure ice VIII ($T\simeq 94$–130 K); (b) amorphous ice *hda* and *lda* ($T\simeq 130$–150 K); (c) cubic ice I*c* ($T\simeq 160$ K) with an intermediate-phase impurity (see d); (d) transitional region I*c*→I*h* (metastable hexagonal phase, $T = 90$ K); (e) hexagonal ice I*h* ($T\geqslant 230$ K). Diffraction peaks from *Al* cryostat walls.

heating of a quenched phase of a high-pressure ice. Typical single neutron-diffraction patterns are also shown in Fig. 2. Experimental data show that the initial phase, ice VIII, remains to a temperature of 130 K. At temperatures 130–135 K the diffraction pattern changes dramatically in 5 min: The narrow peaks corresponding to a crystalline phase of ice vanished and two broad peaks with crests at $d_1 \approx 3.65$ Å and $d_2 \approx 3.00$ Å appeared. The position of these peaks corresponds to the momentum transfer: $Q_1 = 1.72$ Å^{-1} and $Q_2 = 2.09$ Å^{-1}. Figure 3 shows two consecutive neutron-diffraction patterns measured just before the transition (ice VIII) and immediately after it. The peak with a larger d has a structural feature near $Q = 1.63$ Å^{-1}. The values given above are in virtually complete agreement with the values $Q = 1.63$ Å^{-1} and 2.10 Å^{-1} which were measured in Ref. 3 for amorphous phases of high- and low-density ice, while $Q = 1.71$ Å^{-1} corresponds to a (111) reflection for a cubic phase of I*c*.[10] The second peak from the two amorphous phases is situated near $Q = 3.05$ Å^{-1}. Its exact value is difficult to determine because of the fact that there are some diffraction peaks of *Al* in the same region. It should be noted that the diffraction pattern of *hda* is complex in nature, specifically against the background of a broad peak characteristic of amorphous substances we see a small, narrow peak, whose position ($d \approx 3$ Å) does

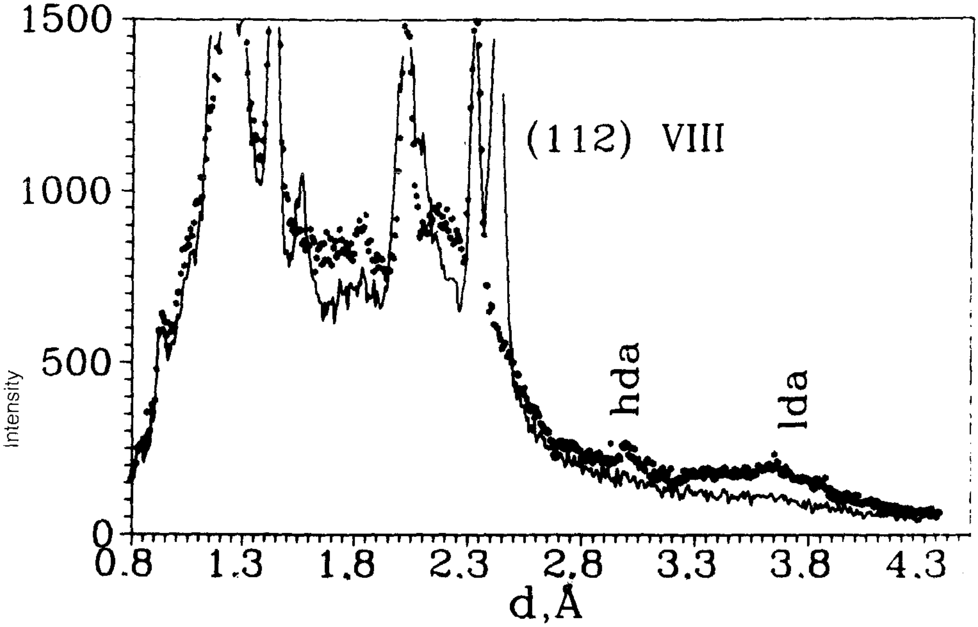

FIG. 3. Two consecutive neutron-diffraction patterns measured upon transition of ice VIII (solid curve) to amorphous phases of ice (points). Narrow persistent peaks correspond to reflections from *Al* cryostat walls.

not correspond to the known structures of ice. The second neutron-diffraction pattern in Fig. 3 therefore corresponds to the coexisting *hda*, *lda*, and fine, crystalline, cubic phases of ice I*c*. There may also be present a new unknown crystalline phase of ice with a structure in which the coordination spheres correspond to a high-density ice.

The mixture of phases remains to ~150–160 K, and at $T = 160$ K a transition to a cubic I*c* phase occurs. The fact that an amorphous ice of two densities coexisted with the temperature-independent positions of Q_1 and Q_2 in our experiment suggests that an *hda*→*lda* transition, if it does exist, is a first-order transition, and not just a relaxation process. We have thus confirmed the validity of the assumption that the transition between different modifications of the amorphous ice is a first-order phase transition. This conclusion was initially drawn by E. Whalley.[11]

A further increase of the temperature causes the cubic phase I*c* to gradually transform to I*h*. It is interesting to note that the peak at (100) of I*h* forms quicker than that at (101) and (102) (Fig. 2). A similar effect was observed in Ref. 12 in the I*c*→I*h* transition of ice in an amorphous matrix of an $LiCl \cdot 10D_2O$ electrolyte. These phenomena can be understood if one takes into account that an fcc→hcp transition is caused by a change in the order of close-packed (111) faces of the cubic phase. At temperatures of 170–210 K we have thus observed the presence of a metastable "hexagonal phase" of ice, in which the planes with a hexagonal close packing of D_2O molecules are uniformly spaced along the *c* axis, $d = d_{002}(\mathrm{I}h) = d_{111}(\mathrm{I}c)$. The order between the hexagonal planes is, however, disrupted and changes constantly from an

ABCABC packing (I*c*) to ABABAB packing (I*h*). Finally, the ice I*h* forms at a temperature of 235 K.

It should be noted that in the study of thermal effects in ice in the sequence of transitions (1), before the onset of the I*c*→I*h* transformation, a distinct knee on the heat-evolution curve, which extended roughly from 190 to 220 K, was observed in Ref. 13. The origin of this knee was attributed in Ref. 13 to the onset of the growth of I*h* from I*c*. In light of the results obtained by us, however, this effect can be explained in terms of the ordering of the close-packed layers of the "hexagonal metastable phase."

In summary, we have been able to observe experimentally for the first time the transition of ice VIII to an amorphous ice *hda*. We have also found that amorphous phases of two densities, *hda* and *lda*, can coexist and that the I*c*→I*h* transition is of a complex nature.

[1] O. Mishima, L. D. Calvert, and E. Whalley, Nature **310**, 393 (1984).
[2] O. Mishima, L. D. Calvert, and E. Whalley, Nature **314**, 76 (1985).
[3] L. Bosio, G. P. Johari, and J. Teixeira, Phys. Rev. Lett. **56**, 460 (1986).
[4] R. J. Hemley, L. C. Chen, and H. K. Mao, Nature **338**, 638 (1989).
[5] D. D. Klug, Y. P. Handa, J. S. Tse, and E. J. Whalley, Chem. Phys. **90**, 2390 (1989).
[6] Y. P. Handa, D. D. Klug, and E. Whalley, Can. J. Chem. **66**, 919 (1988).
[7] A. M. Balagurov, V. B. Zlokazov, G. M. Mironova *et al.*, J.I.N.R. Report P3-89-601, Dubna (1989).
[8] L. F. Vereshchagin, V. M. Bakul', A. I. Semerchan *et al.*, U.S.A. Patent No. 3746484 (1973).
[9] A. M. Balagurov *et al.*, J.I.N.R. Z-84-291, Dubna (1984).
[10] W. F. Kuhs, D. V. Bliss, and J. L. Finney, J. Physique **48**, C1-631 (1987).
[11] E. Whalley, O. Mishima, Y. P. Handa, and D. D. Klug, Annals of the New York Academy of Sciences, **484**, 81 (1986).
[12] A. Elarby-Aouizerat, F. -F. Jal, J. Dupuy, H. Schildberg, and P. Chieux, J. Physique **48**, C1-465 (1987).
[13] Y. P. Handa, O. Mishima, and E. J. Whalley, Chem. Phys. **84**, 2766 (1986).

Translated by S. J. Amoretty