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PHASE TRANSFORMATION OF WATER INTO ICE VII BY SHOCK COMPRESSION

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The results of optical investigations of liquids compressed by several consecutive shock waves are presented. It is shown that if the intensity of the first wave in water is 20–40 kbar, compression by the second wave results in the water-ice VII phase transition. This transition is complete within 10^{-6}–10^{-7} sec and can be observed by the disappearance of the transparency of the compressed layer and the appearance of strong diffuse scattering of light. The relaxation nature of the transition is noted. The effect does not appear in other substances (glycerine, alcohol, and Plexiglas) subjected to double compression, nor does it appear in water compressed only once.

INTRODUCTION

PHASE transformations of water under the action of high pressures into various crystal modifications of ice were observed by Bridgman[1] in his investigations of the isothermal compressibility of water. The behavior of water under shock compression has been investigated by Walsh and Rice[2] and by Al'tshuler and his coworkers.[3] They determined the dynamic adiabat of water and investigated the possibility of a phase transformation into ice under shock compression.

The phase diagram of water is shown in Fig. 1. Up to 40 kbar it is plotted from the data of Bridgman. At pressures higher than 40 kbar the line of phase equilibrium of ice VII and water is plotted according to the data of Pistorius et al.[4] The Hugoniot adiabat in the T – P plane (dash-dot curve) is presented in the work of Rice and Walsh.[5] The temperatures of shock-compressed water which they calculated were experimentally checked by photoelectric pyrometry[1]. The temperatures found experimentally at P ~ 300–400 kbar are sufficiently close to the calculated ones and differ from the latter tending to be about 10 percent lower. This makes it possible to utilize the data of Rice and Walsh for the essential estimates in a broad range of pressures.

It follows from the phase diagram that the dynamic adiabat passes in almost the entire pressure range under consideration (the phase diagram of water was investigated up to 200 kbar[4]) in the region of water, and includes only in the range of pressures from 30 to 45 kbar the region where water and ice VII coexist.[2] These values are approximate, since the Hugoniot adiabat of water on Fig. 1 is plotted without allowance for the fact that it enters into the two-phase water-ice VII region.

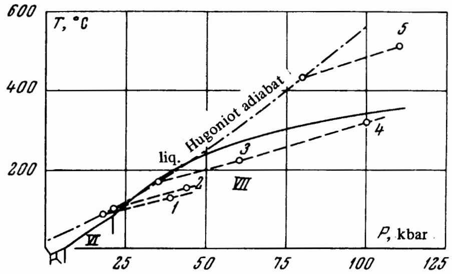

FIG. 1. Phase diagram of water and the location of metastable states 1–4 of the liquid phase in compression by means of two shock waves.

Walsh and Rice[2] investigated the transparency of water in the region of pressures from 30 to 100 kbar. For this purpose they photographed through shock-compressed water a coordinate grid illuminated by an external source of light. The quality of the photograph of the coordinate grid served as a measure of the transparency. In the entire investigated pressure range they observed no disappearance of the transparency of water. Al'tshuler, Bakanova, and Trunin[3] reached other conclusions. Investigating the dynamic adiabat of water up to pressures of about 800 kbar, they observed at P = 115 kbar a jump of the density which they identified with a phase transition in water. This conclusion was also drawn on the basis of experiments in which the transparency of shock-compressed water was investigated by a method close to that of Walsh and Rice.

The optical properties of transparent media compressed by shock waves were investigated in[7]. The region of investigation of the transparency of shock-compressed water was extended to 300 kbar. The authors did not observe a decrease in the intensity of the light reflected by the striker plate (i.e., light which has passed twice through the compressed water) in the entire range of pressures from 40 to 300 kbar. Hence it is concluded, in agreement with[2], that everywhere on the shock adiabat the water remains in the liquid phase.

At the same time, calculations show that one can enter the ice-VII region, or at least the two-phase region, by double compression, if the first shock wave carries pressures of about 20–40 kbar. Such investigations have been undertaken by the authors of this paper.

EXPERIMENTAL METHOD

The investigations were carried out by reflection of light from moving optical boundaries under conditions of an explosion experiment.[7-10] In these experiments a divergent light beam coming from a rectangular illuminated slit was reflected by a system of stationary (reference) optical boundaries as well as from optical

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[1] The measurements were carried out by Sinitsyn, Kuryapin, and by one of the authors of this paper by a method presented in [6].

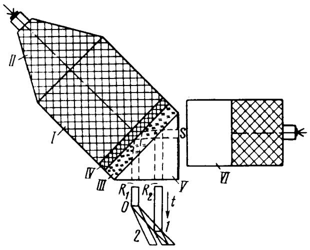

FIG. 2. Schematic diagram of the experiment investigating the reflectivity of the shock-wave front.

boundaries moving parallel to each other (the shock-wave front, the boundary between two compressed media) and entered the objective of a moving-image camera. The registration of the reflection of light from the stationary boundaries with a known relative refractive index made it possible to carry out absolute measurements of the reflectivity of the optical boundaries appearing in the propagation of a shock wave in a transparent medium.

Figure 2 is a schematic diagram of the experiment and of the photographic record (see also Fig. 3b) investigating the reflectivity of the shock-wave front, the index of refraction of the material behind the shock-wave front, and the transparency of the material in the compressed state. The method permits one to measure the reflection coefficient $R \geq 10^{-3}$ with a precision of $\Delta R/R = \pm 8-10$ percent, the index of refraction along the ray path n_{21} with a precision $\Delta n/n = \pm 0.5\%$, and the absorption coefficient α in the range of 1—20 cm^{-1} (from the absorption of light which passed twice through the compressed layer).

The generator of the plane shock wave was a charge of condensed explosive I of 120-mm diameter and 220 mm high, equipped with a lens charge II which transformed the diverging detonation wave into a plane wave. The investigated material III was separated from the charge by a screen IV with known dynamic parameters. A Plexiglas prism V was used to increase the angle of incidence of the light upon the front of the shock wave and to exclude optical boundaries which had a large relative index of refraction. The dimension of the slit S was usually 6—10 mm, and the registration base was ~ 10—15 mm. The slit was illuminated by an argon pulse discharge VI.

On the schematic diagram of the photographic record (Fig. 2) the lines R_1 and R_2 are reference lines; the inclined lines correspond to reflection of light by the shock-wave front propagating along the layer III (the line 0—1) and to reflection by the "piston"—the moving boundary of the two compressed materials IV and III behind the shock front.

The distance between the points 0 and 1 along the t axis corresponds to the time of passage of the shock wave along the investigated material III. If a transparent dielectric served as the screeen IV, then the reflection from the piston was determined by the relative index of refraction of the boundary between the two compressed materials IV and III. When a metallic screen was used, its surface facing the investigated material III was covered in a number of experiments with black nitroenamel. This weakened the reflection from the back boundary, although it also lowered somewhat the quality of the reflection picture from the piston (see Fig. 3d). In other experiments the light was reflected directly by the metallic screen, passing twice through the layer of compressed material. The disappearance of the beam reflected from the piston attested to the nontransparency of the layer.

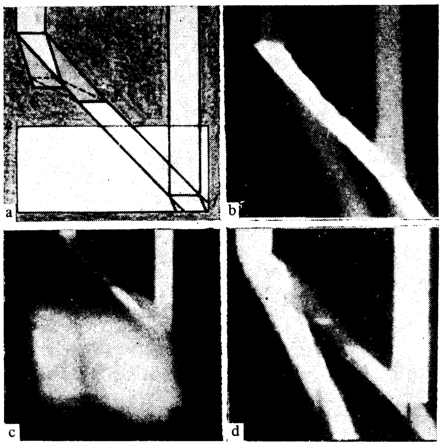

FIG. 3. Recording the phase transformation of water: a—schematic diagram; b—photographic record of the experiment with one shock wave. P = 170 kbar; d—photographic record of the experiment with two shock waves (state 3, see Fig. 1 and the Table); c—photographic record of the experiment demonstrating the phase transformation of water into ice VII (until the beginning of the transformation the water is in state 4, see Fig. 1 and the table).

Compression of the material by several consecutive shock waves was achieved by the use of screens of alternating layers of material: heavy, light, and again heavy. The shock wave passing through such a series of layers splits into a series of waves which overtake one another. The intensity of the first and of the following shock wave was controlled by the choice of the material of the layers, and the place where they overtook one another was controlled by changing their thickness. In our experiments for recording the phase transition we chose such conditions that the intensity of the first wave was 20—40 kbar and the point at which the first wave caught up with the second one was approximately in the middle of the registration base. Figures 3c and 3d show photographic records of experiments recording the overtaking in water. The instant of overtaking is clearly seen from the jumplike change of the reflectivity of the shock-wave front.

THE RECORDING OF THE PHASE TRANSITION IN WATER BY COMPRESSION WITH SEVERAL SHOCK WAVES

A phase transition can be recorded by optical methods when it is accompanied by the appearance of optical inhomogeneities. Light passing through such a medium is attenuated and partly scattered. It is natural to assume that the index of refraction of ice VII differs from that of compressed water and that the appearance of a new phase occurs on a large number of nuclei; therefore the expected photographic record should have the form shown on Fig. 3a. Several series of experiments were carried out in which the pressure of the first shock wave P_1 and the total pressure P_3 after overtaking were varied. The metastable states 1—4 of the liquid phase obtained in double compression of water are indicated on the T — P diagram and in the Table. The photographic record of one of the experiments is shown in Fig. 3c. On it one can discern the following processes (see also the schematic diagram of Fig. 3a). At the instant 0 the shock wave enters the water. At the instant 3 the second shock wave catches up with the first one. After it catches up, the wave is intensified. On the photographic record this is indicated by an increase in its reflectivity (ray 3—1) and the break due to the increase of the velocity. The 0—2 ray corresponds to reflection of light by the piston. At the instant 2 the layer of compressed water becomes nontransparent and the light reflected from the piston is not recorded. Finally, at the instant 4 strong fogging appears on the photographic record indicating that the incident light is scattered diffusely. The loss of transparency of the water and the appearance of diffuse scattering of light can be explained in accordance with the previously made assumption as due to the production of a fine crystalline phase of ice VII with an index of refraction different from that of compressed water which, as follows from the Table, has been recorded in states 1, 2, and 4.

It is characteristic that the loss of transparency of the water does not take place immediately after the exit of the second shock wave from the piston into the water (instant 5) but after some time of the order of a fraction of a microsecond with the fog appearing later. This can obviously be due both to the time relaxation in the production of the ice as well as to the time needed to gather an absorbing layer of sufficient optical thickness. This time is in particular influenced by the fraction of ice particles in the mixture. The same reasons may also influence the delay in the recording of the diffuse scattering.

The relaxation nature of the process is apparently also supported by the results obtained in states 3 and 4 on Fig. 1. Whereas no phase transformation was recorded at lower pressures in the second wave (Fig. 1, point 3 and the photographic record of Fig. 3d), a phase transformation is reliably recorded (point 4 on Fig. 1 and the photographic record of Fig. 3c) with increasing pressure2). It is furthermore clear that with increasing pressure in the first wave we enter a region in which arbitrary states behind the second wave will certainly be in the liquid phase. In this case no phase transition should be recorded which is indeed what was observed experimentally (Fig. 1, point 5).

The experimental results presented attest convincingly to the transition of water into ice under shock compression in a time of 10^{-6}—10^{-7} sec, and the noted relaxation nature of the transition explains the results of[2].

As an additional control we carried out experiments determining the transparency of two-stage compression of alcohol, glycerine, and Plexiglas under the same conditions under which the phase transition in water was observed. No loss of transparency or diffuse scattering of light was detected in any of these substances.

It is interesting to note that in all the investigated substances (water, alcohol, glycerine, and Plexiglas) which remain transparent behind the front of the first shock wave, the second shock wave does not reflect the incident light, although the fact itself that it catches up with the first wave within the investigated layer is clearly seen from the change in the blackening on the photographic record (due to an increase of the reflectivity). An illustrative example of this are the photographic records of Fig. 3c and 3d. This is apparently due to a smearing of the front of the second shock wave. Let us note that even in 1961 Ya. B. Zel'dovich in discussing the results of[11,7] proposed to draw conclusions concerning the viscosity of shock-compressed substances from the reflectivity of the second shock wave propagating through the substance which has undergone preliminary compression by the first shock wave. However, the experiments with water, as well as with other substances, cannot at present provide a unique answer about the reason for the smearing of the second wave. It appears premature to connect this smearing with the viscosity. In order to do this one must relate quantitatively with one another as well as with direct viscosity measurements the following facts: 1) the absence of a "breakdown" of the front of the first wave in water for $P > 80$ kbar[7]; 2) the absence of smearing of the front of the first shock wave in glycerine, alcohol, and other liquids,[12] as well as in water for $P < 80$ kbar[7]; 3) the smearing of the front of the second shock wave in all the investigated substances.

Explosive	Screen (the layer thickness in mm is indicated in parentheses)	P_1, kbar	P_2, kbar	Phase transition	Point No. on figure
TNT	Cu (10) + H_2O (4) + Cu (4) + H_2O (15)	18	39	yes	*1*
TNT	Cu (10) + H_2O (4) + Cu (4) + plexiglas (2) + H_2O (15)	21	44	yes	*2*
TNT	Cu (10) + H_2O (4) + Al (4) + H_2O (15)	35	60	no	*3*
TNT	Cu (10) + H_2O (8) + Al (8) + H_2O (15)	35	100	yes	*4*
Trotylhexog, 50/50	Cu (3) + plexiglas (6) + H_2O (15)	80	110	no	*5*

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2) The phase transformation in point 3 was detected on lowering the initial temperature from +20 to ~ 0°C.

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