Experimental confirmation of the instability of the crystal structure of I*h* ice prior to amorphization under pressure

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The pressure dependences of the propagation velocities of transverse ultrasonic waves were determined for polycrystalline ice I*h* and high-density amorphous ice (*hda*) in the pressure range 0–1.7 GPa at 78 K. It was determined that the velocity of ultrasound decreases significantly ($\sim 10\%$) in I*h* ice polycrystal before amorphization ($T=78$ K, $p=1.1$ GPa) and, correspondingly, the shear modulus softens, which is an experimental indication of mechanical instability of the crystal lattice occurring as a result of solid-phase amorphization under pressure. When the amorphous ice (*hda*) is heated from 78 K at a pressure $p\sim 0.05$ GPa, anomalous behavior of the transverse velocity of ultrasound is observed at temperatures of 100–130 K. This behavior is evidently associated with a phase transition of *hda* into amorphous low-density ice (*lda*). © *1995 American Institute of Physics.*

Many examples of solid-phase amorphization of crystals as a result of a change in pressure have been obtained in the last few years (see, for example, the review in Ref. 1). Ice I*h* is one of the first substances in which this phenomenon was observed, and two modifications of amorphous ice have been discovered: high-density *hda* and low-density *lda*.[2,3] The physical properties of ice at low temperatures have been studied extensively.[2–7]

The amorphorization of ice has stimulated the development of a model of "cold melting," according to which amorphization is regarded as a low-temperature analog of melting, which occurs when the $p-T$ conditions corresponding to continuation of the melting line are reached.[2,3] The concept of "cold melting" has been subjected to serious criticism in a number of studies (see, for example, Ref. 8). A model of "mechanical" or "elastic" instability of the crystal lattice was recently developed to explain solid-phase amorphization.[8–10] It is assumed that amorphization of the crystal is caused by softening of the phonon frequencies and the corresponding elastic moduli in the $p-T$ region which precedes the appearance of disorder. A decrease of the elastic moduli of the crystal by 40–60% before the transformation has indeed been found for alternative methods of solid–phase amorphization (irradiation, anomalous diffusion, pulverization in a ball mill, and others).[11] Evidence favoring the "mechanical-instability" model in the case of amorphization under high pressure has been obtained by means of computer simulation,[10,12]

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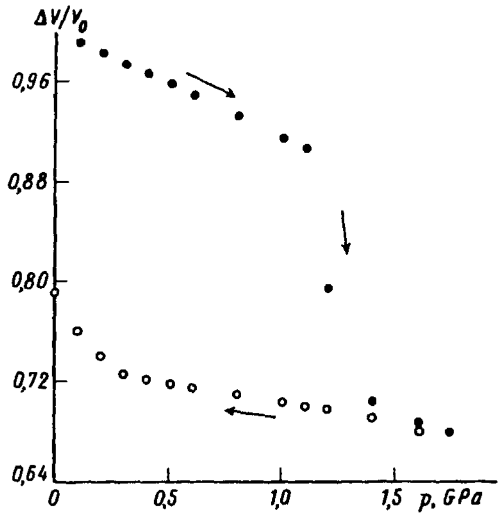

FIG. 1. Relative change in the volume of ice under pressures up to 1.7 GPa and $T=78$ K.

but "softening" (weakening of the bonds in the lattice) before such transitions have not yet been verified experimentally.

The elastic properties of ice I*h* have previously been investigated by the method of Brillouin scattering under pressure up to 0.28 GPa at $T=237.5$ K (Ref. 13) and in ultrasonic measurements up to $p=0.7$ GPa at $T=248$ K (Ref. 14). For low-pressure ice I*h* a negligible (2–3%) decrease of the shear elastic characteristics was observed with changing pressure.

In the present work we have performed the first ultrasonic measurements of the elastic shear moduli of ice at low temperatures ($T=78$ K) in a wide range of pressures. These measurements made it possible to observe the phenomena associated with solid-phase amorphization. The investigations were performed by the pulsed ultrasonic method[15] using quartz piezoelectric transducers with a frequency of 5 MHz on a cylinder-piston-type, high-pressure chamber modified for low-temperature experiments.[16] The ice samples, prepared from distilled water, were $\sim 8-10$ mm high and ~ 16 mm in diameter. The samples were placed in the high-pressure chamber in thin-walled (~ 0.4 mm) lead cylinders and insulated at the ends from the sound piston–ducts by a thin (0.02 mm) copper foil. In the course of the experiment the transit time $t_t(p)$ of a shear ultrasonic wave through the experimental substance and the change in length $l(p)$ of the sample under compression were determined. The I*h*–*hda* transition was determined from the strong change in the two parameters in the pressure range $\sim 1.1-1.3$ GPa. The strongest change in the measured parameters occurred at a pressure of 1.12 ± 0.05 GPa, in complete agreement with the data of Refs. 2–4. Working from the experimental curves $l(p)$ obtained by us, which agree with the published data,[2–7] and taking into account the required experimental corrections,[15] we determined the pressure dependence of the change in volume of ice up to a pressure of 1.7 GPa at $T = 78$ K (Fig. 1). The pressure dependences of the propagation velocity $v_t(p)$ of transverse ultrasonic waves and of the shear modulus

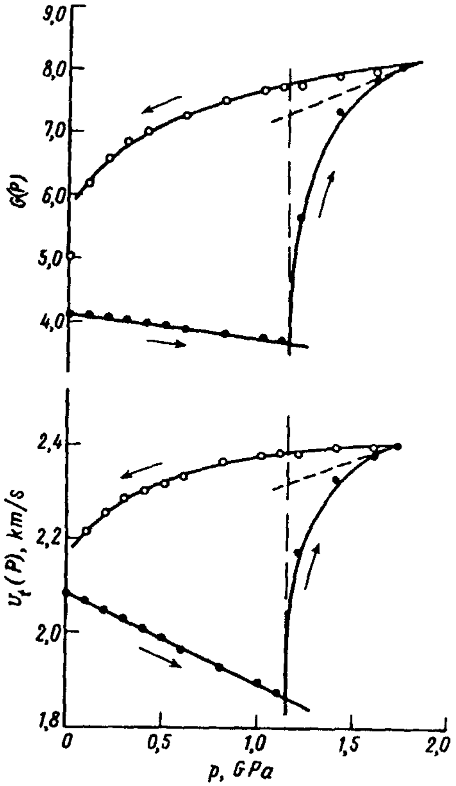

FIG. 2. Pressure dependences of the propagation velocity $v_t(p)$ of transverse ultrasound and the shear modulus $G(p)$ of ice under pressures of up to 1.7 GPa and $T=78$ K. We obtained the value $v_t(0)=2.080\pm0.05$ km/s in special measurements for Ih ice.

$G(p)$ of ice at pressures up to 1.7 GPa at $T=78$ K, calculated from our experimental data for six experiments, are shown in Fig. 2. The changes in $v_t(p)$ and $G(p)$ for ice Ih with increasing pressure to the onset of the transition are anomalous: The derivatives of these quantities with respect to the pressure are negative, indicating that the shear acoustic modes are softened. The polycrystalline shear modulus $G(p)$, calculated from the experimental curves, decreases right to the onset of amorphization ($p=1.0$ GPa) by $\sim 10\%$.

At $p\sim 1.1-1.3$ GPa, the velocity of shear waves increases sharply (by $\sim 19\%$) and the density increases by $20.0\pm0.2\%$. For $p>1.4$ GPa, when the transition can be regarded as essentially completed, the characteristics $v_t(p)$ and $G(p)$ of the amorphous phase of ice (hda) increase almost linearly with pressure. When the pressure is removed, the hda phase remains in a metastable state. A more rapid decrease in $v_t(p)$ and $G(p)$ as $p=0$ could be interpreted as the onset of the reverse transition $hda-lda$ or as a softening of elastic moduli prior to this transformation.

A series of experiments was also performed in the regime of natural heating of hda ice from $T=78$ K at a fixed pressure $p=0.05$ GPa. As the hda ice was heated at

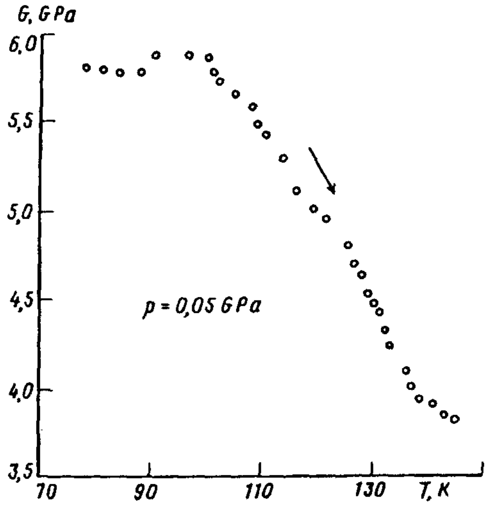

FIG. 3. Shear modulus $G(T)$ with heating of *hda* ice at pressure $p=0.05$ GPa.

$p=0.05$ GPa, anomalies were observed in the behavior of $t_t(T)$ and $l(p)$. These anomalies are apparently associated with transitions of *hda* to a light, amorphous, *lda* phase (at $T\sim 100-130$ K) and then of *lda* to the cubic modification of ice Ic (at $T\sim 140-150$ K). It follows from Fig. 3 that the *hda*–*lda* transition is accompanied by a rapid decrease of the shear modulus $G(T)$ and of the velocity of transverse ultrasound.

According to Ref. 13, a factor of the elastic modulus of I*h* ice $c'=1/2(c_{11}-c_{12})$ softens at $T\sim 237.5$ K by approximately a factor of 1.5–3.0 more rapidly than the polycrystalline shear modulus $G(p)$, which is a combination of the elastic moduli measured for a single crystal.[13,14] If it is assumed that this relation holds at low temperatures and higher pressures, then it can be assumed that the elastic modulus c' decreases by 15–30% prior to amorphization. This value is much lower than the expected softening by 40–60%.[11] However, theoretical calculations have shown that in a number of molecular crystals (for example, SiO_2 and $AlPO_4$) the greatest softening under pressure is observed for *TA* phonons at the boundary of the Brillouin zone,[10] while in ultrasonic measurements the behavior of acoustic phonons is recorded near the center of the Brillouin zone. The behavior of the entire *TA*-phonon branch can be determined by studying the inelastic scattering of neutrons under pressure. We are now conducting such studies, as well as ultrasonic measurements of the elastic properties of ice under different $p-T$ conditions for single-crystal samples.

In summary, we have observed the softening of the shear modulus of an ice polycrystal under low-temperature compression up to the amorphization pressure and at the transition of amorphous high-density ice — amorphous low-density ice.

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