Low-temperature modification of high-pressure ice

T. B. Bizhigitov and N. N. Sirota
Moscow Water Amelioration Institute

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A new modification of ice, ice XII, has been discovered. The boundary of the pressure interval in which this new modification exists is high, between 1200 and 2150 MPa, and the boundary of the corresponding temperature interval is below 90 to 120 K.

We have studied the phase transitions of ice modifications VI, VIII, etc., into a denser modification which we have discovered: ice XII. The changes in the volume of the test sample of ice were measured during isobaric cooling and heating over the temperature range from 90 to 250 K at pressures from 200 MPa to 2150 MPa at intervals of 200–300 MPa and during isothermal increases and decreases in the pressure over the interval from 300 MPa to 3000 MPa at 20-K steps from 90 to 250 K.

The intervals of the temperature and the pressure which we studied here had received essentially no attention in Refs. 1–9, where the basic outlines of the phase diagram of ice were established, or in Ref. 10, where modification XI was discovered.

In the present experiments, the change in the specific volume of the test samples of ice, made from doubly distilled water, is measured in a piston-cylinder pressure chamber. The chamber is cooled with liquid nitrogen. The temperature is monitored by a thermocouple positioned directly in the fluoroplastic cell holding the ice sample. The pressure is calibrated on the basis of the change in the resistivity of manganese, tin, and gallium wires and also on the basis of reference points on the phase diagram of ice. At the beginning and end of each experiment, a calibration is carried out, and the pressure is determined from the change in the resistances of these wires, which are in the measurement cell holding the ice sample.

Figure 1 shows isobars of the relative change in the volume of the test sample over the temperature interval 90–250 K, primarily during cooling and heating. Figure 2

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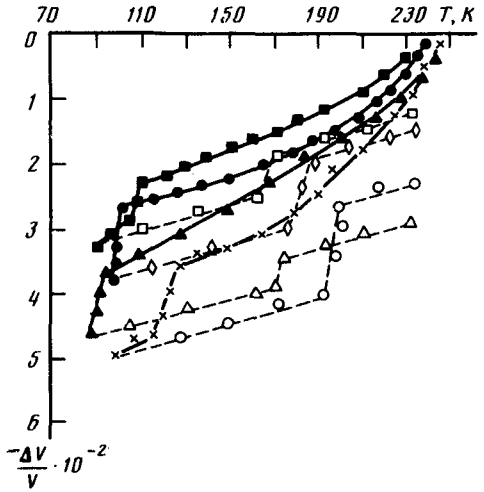

FIG. 1. Isobars of the relative change in volume of the test sample of ice during cooling (at the following pressures: + —1200 MPa; ●—1700 MPa; ▲—1400 MPa; ■—2150 MPa) and during heating (○, ◇, △, □, respectively).

shows an isotherm of the relative change in the volume at 90 K and 106 K as the pressure is raised to 2500 MPa (25 kbar) and then reduced to 300 MPa (3 kbar).

It can be seen from these figures that as it is cooled at constant pressure, the ice sample undergoes a first-order phase transition accompanied by a significant change in volume. This phase transition results in the appearance of a low-temperature modification of high-pressurized ice: ice XII. At pressures of 1200 MPa and 1700 MPa (12 kbar and 17 kbar), the transition from ice VI to ice XII occurs at 90 K and 110 K; the change in specific volume is 20–25%.

At pressures of 1400 MPa and 2150 MPa (14 kbar and 21.5 kbar), ice XII forms at temperatures of 100 K and 120 K, respectively; the change in specific volume is 25–30%.

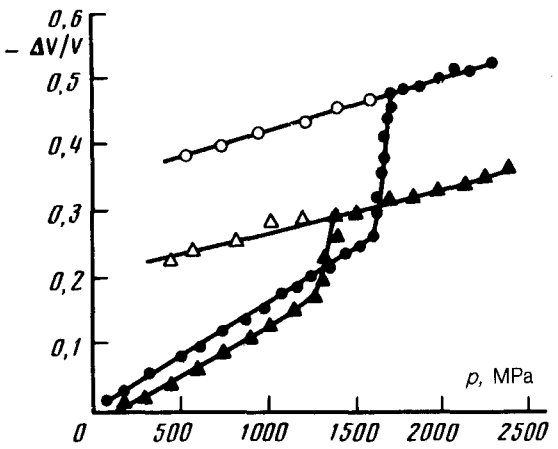

FIG. 2. Isotherms of the relative change in volume as the pressure is raised (▲—90 K; ●—106 K) and as the pressure is lowered (△—90 K; ○—106 K).

During isothermal compression at 90 K and 106 K of ice cooled to the specified temperature at a low pressure, we observe the phase transition $1h \rightarrow$ XII at pressures of 1200 MPa and 1600 MPa (12 kbar and 16 kbar), respectively, accompanied by a change in volume of 30–35% of the original volume. At these temperatures, as the pressure is lowered, we do not observe the inverse transition XII $\rightarrow 1h$. The modification of ice XII persists as the pressure is completely removed (a similar "quenching" effect had been observed previously for ice modifications VI and VIII below 80 K).

These experimental results furnish evidence of a transition of the initial modifications of ice VI and VIII and also of ice $1h$ into a new, much denser modification, ice XII.

During cooling, the interval over which ice XII exists on the phase diagram of ice lies below the line connecting the points 90 K at 1200 MPa (12 kbar) and 120 K at 2150 MPa (21.5 kbar). These have also been the first experiments on the effect of a change in the temperature at constant pressure on the phase diagram of ice. The results clearly reveal the appearance of a new, dense modification of ice: ice XII.

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