CRYSTAL STRUCTURE AND COMPOSITION OF HYDROGEN HYDRATE C1

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Introduction

In 1993, an investigation of the H_2O-H_2 system in the pressure interval 7.7 to 300 kbar revealed the occurrence of two crystalline hydrogen hydrates [1]. These were the rhombohedral C1 phase stable at pressures up to 25.5 kbar and cubic C2 phase stable at higher pressures. The C1 phase was examined by X-ray diffraction at a pressure of 21 kbar and a temperature of 22ºC. The water sublattice of the C1 phase was shown to be similar to the rhombohedral structure of high-pressure ice II with the cages filled by hydrogen molecules. On the basis of results of Raman studies, the molar ratio H_2/H_2O of the C1 phase was assumed to be invariable at pressures 7.7–25.5 kbar and equal to 1/6 that corresponds to 1.8 wt.% H_2. A few years later, in the year of 1999, a cubic clathrate hydrate sII was found to form in the H_2O-H_2 system at pressures from 1.0–3.6 kbar [2]. Further investigations established the crystal structure of this hydrate [3] and the boundaries of its stability in composition [3,4] and pressure and temperature [5].

In the work of ref. [5], the sII→C1 transition was studied using a volumetric technique and the hydrogen content of the C1 phase was estimated under the assumption that – by analogy with the He-H_2O system [6] – the absorption of molecular hydrogen did not change the volume of ice II.

Phase relations in the H_2O-H_2 system are of significant interest, in the first place, for planetary science because hydrogen and water are among the basic building materials of many planets. Our present studies were aimed at the synthesis of the C1 phase, investigation of its crystal structure at ambient pressure, direct measurement of its hydrogen content and the volume effect of hydrogen uptake.

Results and discussion

A sample of the C1 phase weighing a few tens milligrams was synthesized from the liquid at a hydrogen pressure of 18 kbar and room temperature and quenched under pressure to the temperature of liquid nitrogen. Using hot extraction in vacuum, the sample was shown to contain 1.0 wt.% H_2 (curve **a** in Fig. 1).
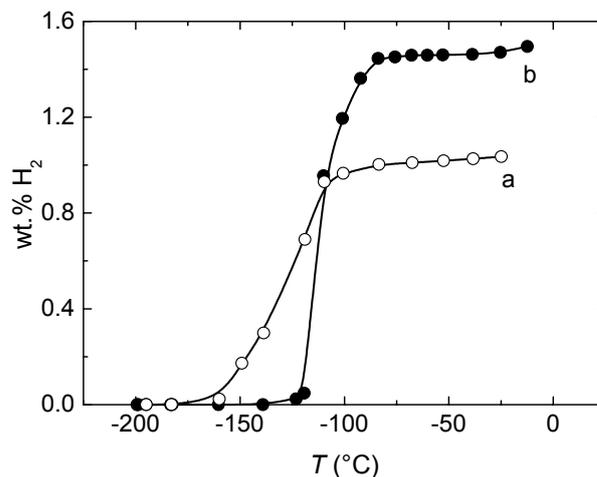

Fig. 1. Hydrogen desorption from quenched H_2O-H_2 samples in the course of heating in a pre-evacuated volume at a rate of about 25°C/min. The samples were produced from the liquid under a hydrogen pressure of 18–20 kbar and quenched to the liquid nitrogen temperature after one (**a**) and five (**b**) cycles of cooling and heating across the crystallization and melting lines of ice VI.

The phase composition and structure of water sublattices of phases in the quenched H_2O-H_2 sample were examined by X-ray diffraction at ambient pressure and a temperature of –193°C. As seen from the diffraction pattern in Fig, 2, the sample consisted of the C1 phase, the high-pressure phase of ice VI and of a minor amount of the low-pressure phase of ice Ih condensed on the sample surface while it was loaded into the X-ray cryostat.

At ambient pressure, the quenched C1 phase had the structure of ice II with the parameters a = 7.8 Å и α = 113.2º of the rhombohedral unit cell that were close to the parameters of ice II without hydrogen [7]. The molar volume of the C1 phase at a temperature of –193ºC and ambient pressure was equal 15.34 cm^3 that was also close to a value of 15.32 cm^3 for ice II without hydrogen under similar conditions (P = 1 atm., T = –175ºC). This can be considered as direct experimental evidence in favour of our assumption [5] that the incorporation of molecular hydrogen in the lattice of ice II nearly does not change its parameters.
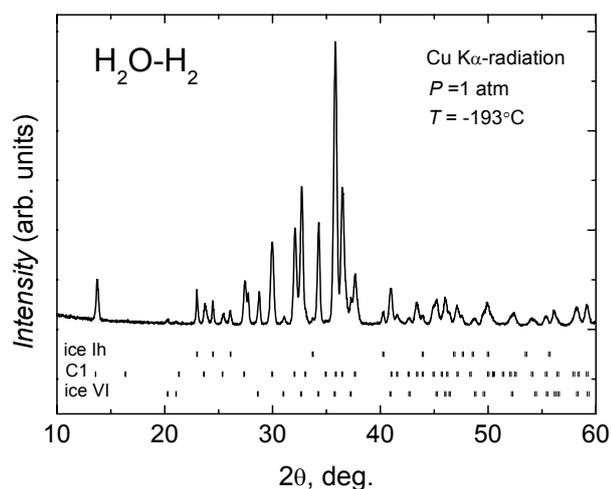
Fig. 2. X-ray diffraction pattern of the C1 sample synthesized at a hydrogen pressure of 18 kbar and room temperature.

According to the X-ray results, the quenched sample contained approximately equal amounts of C1 hydrate and ice VI, which – in the absence of hydrogen – would have been the stable phase under the chosen T-P conditions of synthesis of the C1 phase. Assuming that there was no hydrogen in the ice VI found in the quenched sample, this gives the hydrogen content about 2 wt.% for the C1 phase, which corresponds to the molar ratio $H_2/H_2O \approx 1/6$ in agreement with the estimate in ref. [1].

Earlier we found out [8] that sII hydrate can only crystallize from the liquid together with ice Ih, which would be stable in the absence of hydrogen under the T-P conditions of synthesis of the sII phase. In order to examine if C1 hydrate crystallizes together with ice VI or not, we carried out a volumetric investigation of melting and crystallization of the C1 phase at hydrogen pressures up to 8 kbar and temperatures from –17 to +30ºC.

Representative experimental isochors are shown in Fig. 3. The melting of the C1 hydrate preliminarily produced from sII hydrate via a solid-state reaction was accompanied by a step-wise increase in pressure. Further cooling of the liquid thus formed was followed by the pressure drop at temperatures a few degrees below the melting line of ice VI [9]. This corroborates the assumption about the simultaneous crystallization of the C1 phase and ice VI.

Conclusions

Our recent experiments have shown [10] that cycling across the melting line of ice Ih in
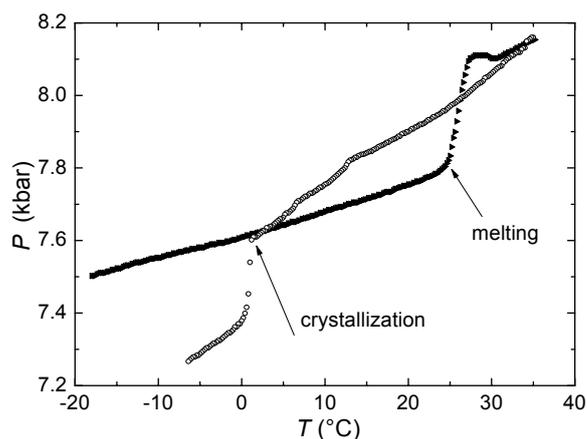

Fig. 3. Isochors of melting and crystallization of the C1 phase in the H_2O-H_2 system. The solid triangles correspond to the heating of the system and the open triangles to the cooling.

the stability range of sII hydrate increased the total content of the sample from 18 to 80%. We performed 5 cycles of heating and cooling of a water sample in the temperature range from 20 to 84ºC at a hydrogen pressure of 20 kbar. In doing so, we crossed the melting and crystallization lines of ice VI, but we never melted the C1 hydrate. As seen from Fig. 1, the cycling did result in the increase in the mean hydrogen concentration of the sample to 1.5 wt.% that corresponded to the content of the C1 phase in the order of 80%.

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