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## New phase in the water-hydrogen system

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## ABSTRACT

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## 1. Introduction

Until recently, three hydrogen-rich crystalline phases,  $C_1$  [1],  $C_2$  [1] and sII [2], have been known in the  $H_2O-H_2$  system. These phases are called hydrogen clathrate hydrates, and their crystal structures are networks of hydrogen-bonded  $H_2O$  molecules encasing guest  $H_2$  molecules that only weakly interact with the network by van der Waals forces [1,2]. The available experimental data on phase relations in water placed in an atmosphere of molecular hydrogen are presented in Fig. 1. The inaccuracy in the equilibrium phase boundaries of the sII field does not exceed the lines thickness. To illustrate the accuracy and measuring methods used to construct the boundaries of the  $C_1$  and  $C_2$  fields at higher hydrogen gen pressures, experimental points are shown in Fig. 1 along with the lines.

The equilibrium hydrogen solubility in the low-pressure hexagonal ice-I<sub>h</sub> is small and only reaches a molecular ratio H<sub>2</sub>/H<sub>2</sub>O of  $X_{I_h} = 0.011(5)$  near the triple point of the Liq.+I<sub>h</sub>+sll equilibrium at P = 1.07(5) kbar and  $T = -10(1)^{\circ}$ C [3]. The hydrogen content of the cubic sll hydrate varies with pressure and temperature from  $X_{sll} = 0.21(1)$  near the Liq.+I<sub>h</sub>+sll triple point [3] to  $X_{sll} = 48/136 \approx 0.35$  at P = 2 kbar and  $T < -90^{\circ}$ C [4]. The C<sub>2</sub> phase has a diamond-like H<sub>2</sub>O sublattice and  $X_{C_2} = 1$  at hydrogen pressures from 23 to 300 kbar [1].

A new hydrogen hydrate denoted C<sub>0</sub> is discovered in the H<sub>2</sub>O–H<sub>2</sub> system at -20 °C and hydrogen pressures near 5 kbar. Powder samples of the hydrate were quenched under high pressure to the liquid N<sub>2</sub> temperature and recovered to ambient pressure. Hot extraction in vacuum demonstrated that the hydrogen release from the quenched samples started immediately on heating above 77 K and completed at about 170 K. The total amount of the released hydrogen reached a molecular ratio of H<sub>2</sub>/H<sub>2</sub>O  $\approx$  0.13. An X-ray diffraction investigation at 80 K showed that the samples were single-phase and had a trigonal structure with *a* = 6.33 Å and *c* = 6.20 Å on hexagonal axes.

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The C<sub>1</sub> hydrate can be considered as H-filled high-pressure ice-II with a rhombohedral structure [1]. The hydrogen content of the C<sub>1</sub> phase at room temperature and hydrogen pressures 7.5–23 kbar lies in the range  $X_{C_1} = 0.1-0.25$ , the most likely value being  $X_{C_1} =$  $1/6 \approx 0.17$  [1]. Assuming that the triple point at 3.6(1) kbar and +1(1)°C represents the Liq.+sII+C<sub>1</sub> equilibrium [5,6], volumetric results of Ref. [6] gave  $X_{sII} = 0.32(2)$  and  $X_{C_1} = 0.10(2)$  near this point and along the sII  $\leftrightarrow$  C<sub>1</sub> line at temperatures down to -22°C.

The sll  $\leftrightarrow$  C<sub>1</sub> transformation is rather unusual, because it is accompanied by a decrease of the equilibrium hydrogen solubility in the solid phase at increasing pressure. The resulting emission of gaseous hydrogen is of interest, in the first place, for planetary science, as hydrogen and water are among the basic building materials of many icy satellites, and the sll  $\leftrightarrow$  C<sub>1</sub> transformation could play a key role in their evolution.

To directly determine the hydrogen content of the C<sub>1</sub> hydrate, we have recently synthesized H<sub>2</sub>O–H<sub>2</sub> samples from the liquid at a hydrogen pressure of 18 kbar and room temperature (open triangle in Fig. 1) and quenched them under pressure to the temperature of liquid nitrogen [7]. An X-ray study showed the samples to be composed of a mixture of C<sub>1</sub> 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 C<sub>1</sub> phase. Assuming that there was no hydrogen in the ice-VI phase, hot extraction gave  $X_{C_1} \approx 1/6$  for the C<sub>1</sub> phase [7] in agreement with the estimate in Ref. [1].

In the present work, we initially planned to complete the investigation of phase relations in the  $H_2O-H_2$  system by studying the hydrogen content and crystal structure of  $C_1$  samples synthesized near the line of the sII  $\leftrightarrow C_1$  transformation (the synthesis conditions are shown by the open rhombs in Fig. 1) and quenched to the N<sub>2</sub> temperature. Quite unexpectedly, we produced a new hydrate

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**Fig. 1.** *T*–*P* diagram of phase transitions in the H<sub>2</sub>O–H<sub>2</sub> system with the H<sub>2</sub> gas taken in access. The thick solid curves at hydrogen pressures below 3.6 kbar show the melting lines of the I<sub>h</sub> and sII phases determined by DTA [5] and later, more precisely by volumetric measurements [3], and also the lines of the I<sub>h</sub>  $\leftrightarrow$  sII [3,5] and sII  $\leftrightarrow$  C<sub>1</sub> (?) [6] equilibria determined by volumetry. The melting temperatures of hydrates at higher hydrogen pressures were determined by DTA (symbols 1 represent results of [5]) and by optical microscopy in diamond anvils (2 and 3 are results of [1]). Symbols 4 show the points of the C<sub>1</sub>  $\rightarrow$  C<sub>2</sub> transition by optical microscopy [1]. Solid triangles 5 indicate the points of the *in situ* X-ray identification of the C<sub>1</sub> phase [1]. Open triangle 6 indicates the synthesis conditions of the quenched C<sub>1</sub> sample examined by X-ray diffraction in Ref. [7]; its X-ray pattern is presented in Fig. 2 b. Open rhombs 7 show the synthesis conditions of the C<sub>0</sub> samples quenched and studied in the present work.

with the structure never observed in the high-pressure ices or gas hydrates studied so far.

#### 2. Experimental details

Three samples of the new hydrate denoted C<sub>0</sub> were produced using a manostatic device [8] made of beryllium bronze, with an inner diameter of 8 mm, in which gaseous hydrogen was compressed by a moving piston. The hydrogen pressure was measured with an accuracy of  $\pm 0.5$  kbar, the temperature  $\pm 3 \,^{\circ}$ C. The samples were made of distilled water frozen and powdered in an agate mortar under liquid nitrogen prior to the high-pressure experiment in order to speed up the kinetics of hydrogen absorption. Approximately 300 mg of the powder was placed into the highpressure chamber cooled to -20 °C and the chamber was filled with gaseous hydrogen under a pressure of 1.5 kbar. The hydrogen pressure was then raised to 2.5 kbar at -20 °C and kept constant for 30 min that transformed the sample to the sII phase [6]. The gas was further compressed to a pressure near 5 kbar (open rhombs in Fig. 1) and kept constant for 1 h. According to Ref. [6], the procedure used should have completely transformed the sample to the higher hydrate, which was expected to be the C1 phase. After the hydrogenation was over, the manostat was immersed in liquid nitrogen, cooled to 77 K in about 3 min and disassembled. When not in use, the H<sub>2</sub>O-H<sub>2</sub> samples thus produced were stored in liquid N<sub>2</sub> to avoid hydrogen losses.

The crystal structure of the obtained  $H_2O-H_2$  samples was studied by powder X-ray diffraction at ambient pressure and 80 K using a Siemens D500 diffractometer equipped with a home-designed nitrogen cryostat that permitted loading the powder samples without their intermediate warming. The diffraction data were analyzed with a computer program [9] based on the Rietveld profile refinement technique. The hydrogen content and thermal stability of the samples were examined by hot extraction into a pre-evacuated volume.



**Fig. 2.** X-ray diffraction patterns of  $H_2O-H_2$  samples measured at ambient pressure and T = 80 K using Cu  $K_{\alpha}$  radiation. (a) The C<sub>0</sub> sample from the present work; the upper curve is the profile fit to the experimental pattern (open circles) and the lower curve shows the difference between this pattern and the fit (see text); (b) the C<sub>1</sub> sample (a mixture of 60 vol.% C<sub>1</sub> and 40 vol.% ice-VI) from Ref. [7]. Pattern (b) also shows a contribution from a minor amount of the low-pressure phase of ice-I<sub>h</sub> condensed on the sample surface while it was loaded into the X-ray cryostat.

The studies of the quenched  $H_2O-H_2$  samples were supplemented by *in situ* volumetric measurements of an isotherm at -18 °C and an isochor at hydrogen pressures near 6 kbar using a piston-cylinder high-pressure chamber with an inner diameter of 12 mm [10]. The pressure was measured with an accuracy of  $\pm 0.03$  kbar, the temperature  $\pm 0.5$  °C, the volume  $\pm 1$  mm<sup>3</sup>. The procedure applied to convert the starting powder of ice-I<sub>h</sub> to the sII phase was the same as in the case of the manostatic device. After the formation of the sII phase at 2.5 kbar at -20 °C was completed, the volume and the temperature in the chamber were varied as required.

## 3. Results and discussion

Fig. 2 shows an X-ray diffraction pattern of one of the  $H_2O-H_2$  samples prepared in the present work (a) and, for comparison, a pattern of a C<sub>1</sub> sample from Ref. [7] (b). The C<sub>1</sub> sample was composed of a mixture of approximately equal amounts of the C<sub>1</sub> phase and high-pressure ice-VI, and was also contaminated with ice-I<sub>h</sub> condensed on the surface of the sample when it was loaded into the X-ray cryostat. As one can see, our new  $H_2O-H_2$  sample did not contain the C<sub>1</sub> phase or ice-VI. The ice-I<sub>h</sub> impurity manifested itself by three weak lines at  $2\theta = 22.8$ , 24.3 and 25.9°. The sample holder gave a week line at  $2\theta = 27.6^\circ$ . All other lines in Fig. 2a can be indexed to a hexagonal unit cell with *a* = 6.33 Å and *c* = 6.20 Å. The (00 *l*) lines with *l* = 1, 2 and 4 are absent that implies the reflection condition *l*= 3*n*, where *n* is an integer. None of the known phases of ice or gas hydrates can give such a diffraction pattern.

The diffraction patterns of other two  $C_0$  samples studied in the present work looked similar. However, the unit cell parameters of different samples did not fully coincide and differed within  $\pm 0.01$  Å. The line intensities also varied from sample to sample, so the crys-

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tal structure of the  $C_0$  phase could not be reliably determined on the basis of the available powder diffraction results. Our very preliminary results of a profile analysis of the measured X-ray patterns can be described as follows.

The l = 3n extinction condition is satisfied for six trigonal space groups, which can be considered in pairs:  $P_{3_1}$  and  $P_{3_2}$ ;  $P_{3_1}21$  and  $P_{3_2}21$ ;  $P_{3_1}12$  and  $P_{3_2}12$ . The groups in each pair differ from each other only by the direction of the screw axis rotation. This direction is indistinguishable from the powder diffraction data, so we restricted ourselves to only three groups,  $P_{3_1}$  and  $P_{3_1}12$  and  $P_{3_1}21$ . We started modelling the structure of the  $C_0$  phase using the more symmetrical  $P_{3_1}12$  and  $P_{3_1}21$  groups. The  $P_{3_1}12$  group provided a significantly better agreement with the experimental data than the  $P_{3_1}21$  group, so the  $P_{3_1}21$  group was ruled out. Using the  $P_{3_1}$  group and, correspondingly, varying 9 positional parameters instead of 3 did not noticeably improved the fit, so we had no reason to assume that the symmetry of the  $C_0$  structure was lower than  $P_{3_1}12$ .

The proposed description of the oxygen sublattice in the space group P3<sub>1</sub>12 allowed the most satisfactory fit to the line intensities for all three studied C<sub>0</sub> samples and gave a reasonable value of 2.78 Å for the O–O interatomic distances. The profile fit shown in Fig. 2a by the thin solid curve is calculated assuming that the oxygen atoms occupy three types of crystallographically non-equivalent positions in the unit cell of the C<sub>0</sub> phase. These are the 3a<sub>1</sub> positions with the positional parameter x = 0.23 and occupancy  $\omega = 1$ ; the 3b positions with x = 0.75 and  $\omega = 1$  and the half-filled  $3a_2$  positions with x = 0.10 and  $\omega = 0.5$ . The 6 oxygen atoms/unit cell occupying all  $3a_1$  (x = 0.23) and 3b (x = 0.75) sites form channels along the *c*-axis. These channels accommodate the half-filled 3a<sub>2</sub> oxygen sites and one can expect that these 3a<sub>2</sub> sites serve as stoppers transforming the channels into the chains of voids. If every such void is occupied with one H<sub>2</sub> molecule, the hydrogen content of the hydrate reaches an  $H_2/H_2O$  ratio of 1.5/7.5 = 0.2. The total number of the oxygen atoms in the unit cell of the C<sub>0</sub> phase, 7.5 atoms/unit cell, corresponds to a density of about  $1 \text{ g/cm}^3$ .

We find it necessary to note again that the results of profile analysis discussed above can only be considered as preliminary ones. The fitting parameters were chosen so as to equally well describe three diffraction patterns of different C<sub>0</sub> samples. The line intensities in these patterns being different, this gave us rather poor profile factors of  $R_{\text{prof}} = 14\%$ ,  $R_{\text{wp}} = 18\%$  and  $\chi = 0.14$  with the expected  $R_{\text{ex}} = 5\%$ . Nevertheless, we believe that the proposed  $P3_112$  model reflects some intrinsic features of the C<sub>0</sub> structure and could make a starting point for its future refinements.

Fig. 3 demonstrates a significant difference in the thermal stability of the C<sub>0</sub> and C<sub>1</sub> phases in vacuum. If heated at 25 °C/min, the C<sub>1</sub> phase starts evolving hydrogen at  $\approx$ 140 K and completely decomposes at  $\approx$ 200 K. The hydrogen release from the C<sub>0</sub> phase begins immediately on heating above 77 K and completes at  $\approx$ 170 K. The maximum amount of hydrogen evolved from the C<sub>0</sub> samples reached X<sub>C0</sub> = 0.13. However, in view of the instability of the samples at a nearly N<sub>2</sub> temperature, the equilibrium hydrogen content of the C<sub>0</sub> phase could be higher under the synthesis conditions (P<sub>H2</sub>  $\approx$  5 kbar and T=-20 °C). In particular, it could reach X<sub>C0</sub> = 0.2 corresponding to the complete H<sub>2</sub> filling of voids in the proposed P3<sub>1</sub>12 water sublattice of this hydrate.

It is interesting to mention that a heating of the  $C_0$  sample to 100 K for 10 min, which removed the major portion of the hydrogen (see Fig. 3a), did not change the intensity distribution in its X-ray pattern at 80 K compared to that measured before the heating, and the lattice parameters of the  $C_0$  phase only decreased by about 0.01 Å. After further heating to 140 K resulting in the loss of nearly all hydrogen, the  $C_0$  phase transformed to metastable cubic ice I<sub>c</sub>.

According to the T-P diagram of the  $H_2O-H_2$  system presented in Fig. 1, the  $C_0$  phase was synthesized inside the stability range of



**Fig. 3.** Hydrogen release from  $H_2O-H_2$  samples in the course of heating in a preevacuated volume at a rate of 25 °C/min. (a) The C<sub>0</sub> sample from the present work; (b) the C<sub>1</sub> sample (a mixture of 80 vol.% C<sub>1</sub> and 20 vol.% ice-VI) from Ref. [7]. Both samples were quenched to the liquid nitrogen temperature after a 1 h exposure to the hydrogen pressures and temperatures indicated in the figure.

the  $C_1$  phase. We think that the diagram is incomplete. It should include the stability region of the  $C_0$  phase, and our samples were synthesized inside this region.

In any case, it is very unlikely that the C<sub>1</sub> phase was formed at  $\approx$ 5 kbar and -20 °C and then transformed to the C<sub>0</sub> phase in the course of lowering the temperature to 77 K and pressure to 1 bar. In the first place, a similar procedure saved the C<sub>1</sub> phase in the samples prepared at a higher pressure of 18 kbar and +20 °C [7], therefore no  $C_1 \rightarrow C_0$  transformation could occur at liquid N<sub>2</sub> temperature and lower pressures. Secondly, the diffraction patterns of the C<sub>0</sub> samples showed no traces of the C<sub>1</sub> phase, while the complete  $C_1 \rightarrow C_0$ transformation in the course of the rapid cooling to the liquid N<sub>2</sub> temperature was not likely. Finally, as seen from Fig. 4, cooling the  $C_1$  phase from 5 kbar and -20 °C brings it into the stability region of ice-II in the *T*–*P* diagram of water without hydrogen [11]. The C<sub>1</sub> phase is actually ice-II filled with H<sub>2</sub> molecules weakly interacting with the H<sub>2</sub>O network [1]. Consequently, even if the C<sub>1</sub> phase lost some hydrogen at decreasing hydrogen pressure, its H<sub>2</sub>O sublattice would have remained unchanged rather than transformed to a new structure, the more so that ice-II without hydrogen can be recovered to ambient pressure at liquid nitrogen temperature [12].

To know more about the *T*–*P* stability region of the C<sub>0</sub> phase, we supplemented volumetric results of Refs. [6,7] with measurements of an isotherm at -18 °C and hydrogen pressures up to 8 kbar and an isochor at pressures near 6 kbar. Both curves are shown in Fig. 5. The isochor is also plotted in Fig. 4 together with isochors measured in Refs. [6,7].

P-V isotherms in the H<sub>2</sub>O-H<sub>2</sub> system were earlier measured at pressures up to 4.7 kbar [6]. Similar to those, the isotherm presented in Fig. 5 was constructed in the regime of a step-wise increase in the total volume, V, of the system. Changing the volume led to a temporal drift of the pressure. The drift lasted about

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Fig. 4. T-P diagram of phase equilibria in the H<sub>2</sub>O-H<sub>2</sub> system (thick solid lines) superimposed onto the diagram of H2O [11] (dashed lines; phase fields are labelled with the encircled symbols). The thin solid curves represent isochors in the H<sub>2</sub>O-H<sub>2</sub> system measured at increasing temperature: 1 - Ref. [6]; 2 - Ref. [7]; 3 - present work (see Fig. 5). Open rhombs show the synthesis conditions of the C<sub>0</sub> samples quenched and studied in the present work (same as in Fig. 1).



Fig. 5. Variation of volume of the  $H_2O-H_2$  system at -18 °C and increasing hydrogen pressure (the isotherm, left scale) and variation of pressure at constant volume on heating at a rate of 0.1 °C/min (the isochor, right scale).

20 min in the interval of the phase transition at  $P_{\rm H_2} \approx 3.8$  kbar and <5 min outside this interval. The volume was held constant until the hydrogen pressure stopped changing, and the final value was plotted in the figure.

As one can see from Fig. 5, the isotherm measured at -18 °C and pressures 2.5–8 kbar only shows one discontinuity at  $P_{\rm H_2} \approx$ 3.8 kbar attributable to a phase transformation. This can only be the sII  $\rightarrow$  C<sub>0</sub> transformation and not sII  $\rightarrow$  C<sub>1</sub> as considered earlier [6]. As seen from Fig. 4, the isochors constructed at pressures from  $\approx$ 4.5 to  $\approx$ 7.5 kbar and  $T \ge -18$  °C only have steps near the melting curve. These suggest that the C<sub>0</sub> phase is formed from the sII phase and does not transform to the C1 phase at hydrogen pressures up to 7.5 kbar and temperatures from  $-18\,^\circ\text{C}$  to the melting curve. Correspondingly, the triple point at 3.6(1) kbar and  $+1(1)^{\circ}$ C, which was earlier considered to be the point of the Liq. + sII + C1 equilibrium [5,6], is the invariant Liq. +  $sII + C_0$  point. The line radiating downwards from this point in the T-P diagram of the H<sub>2</sub>O-H<sub>2</sub> system (Figs. 1 and 4) is the equilibrium line of the reversible sII  $\leftrightarrow C_0$ transformation.

Results of the present paper show that the C<sub>0</sub> phase is stable below the melting curve, which ascends to  $\approx 25 \,^{\circ}$ C at 7.5 kbar. According to [1], the C<sub>1</sub> phase is stable at temperatures above 22(3) °C and pressures above 7.5 kbar. The line of the  $C_0 \leftrightarrow C_1$  transformation should therefore cross the melting curve at a pressure near 7.5 kbar. If the available experimental melting points of ices in a hydrogen atmosphere shown in Fig. 1 are fitted by smooth curves separately at pressures below 8 kbar and above 6 kbar, this gives a bent at  $\approx$ 7 kbar and  $\approx$ 20 °C (see thin solid curves in Figs. 1 and 4). One can speculate that this is the triple point of the Liq.  $+C_0 + C_1$ equilibrium. (Note that the suggested location of the triple point at a pressure of 7 kbar does not contradict the observed absence of the  $C_0 \rightarrow C_1$  transformation at pressures up to 7.5–8 kbar because of the baric hysteresis characteristic of phase transformations between different hydrogen hydrates [3,6].)

## 4. Conclusions

A new hydrate denoted C<sub>0</sub> is discovered in the H<sub>2</sub>O-H<sub>2</sub> system. The trigonal crystal structure of this hydrate has no analogue among the structures of high-pressure phases of ice and the large variety of gas hydrates studied so far. The occurrence of the C<sub>0</sub> hydrate necessitated a revision of the T-P diagram of the  $H_2O-H_2$ system in the pressure range of a few kilobars. Our experimental results suggest that the C<sub>0</sub> hydrate is stable in the T-P region below 8 kbar, which was earlier considered as part of the stability field of the C<sub>1</sub> hydrate. Constructing the high-pressure boundary of the C<sub>0</sub> stability field requires further in situ measurements at hydrogen pressures above 8 kbar and temperatures below -20 °C. The work on extending the operability of our volumetric technique to this T-P range is in progress.

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