



New phase in the water–hydrogen system

V.S. Efimchenko^{a,*}, M.A. Kuzovnikov^a, V.K. Fedotov^a, M.K. Sakharov^a, S.V. Simonov^a, M. Tkacz^b

^a Institute of Solid State Physics RAS, 142432 Chernogolovka, Moscow District, Russia

^b Institute of Physical Chemistry PAS, Kasprzaka 44/52, 01-224 Warsaw, Poland

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ABSTRACT

A new hydrogen hydrate denoted C_0 is discovered in the H_2O – H_2 system at -20°C and hydrogen pressures near 5 kbar. Powder samples of the hydrate were quenched under high pressure to the liquid N_2 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 $H_2/H_2O \approx 0.13$. An X-ray diffraction investigation at 80 K showed that the samples were single-phase and had a trigonal structure with $a = 6.33 \text{ \AA}$ and $c = 6.20 \text{ \AA}$ on hexagonal axes.

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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 enclosing 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 pressures, experimental points are shown in Fig. 1 along with the lines.

The equilibrium hydrogen solubility in the low-pressure hexagonal ice- I_h is small and only reaches a molecular ratio H_2/H_2O of $X_{I_h} = 0.011(5)$ near the triple point of the $\text{Liq.} + I_h + \text{sII}$ equilibrium at $P = 1.07(5) \text{ kbar}$ and $T = -10(1)^\circ\text{C}$ [3]. The hydrogen content of the cubic sII hydrate varies with pressure and temperature from $X_{\text{sII}} = 0.21(1)$ near the $\text{Liq.} + I_h + \text{sII}$ triple point [3] to $X_{\text{sII}} = 48/136 \approx 0.35$ at $P = 2 \text{ kbar}$ and $T < -90^\circ\text{C}$ [4]. The C_2 phase has a diamond-like H_2O sublattice and $X_{C_2} = 1$ at hydrogen pressures from 23 to 300 kbar [1].

The C_1 hydrate can be considered as H-filled high-pressure ice-II with a rhombohedral structure [1]. The hydrogen content of the C_1 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 $+1(1)^\circ\text{C}$ represents the $\text{Liq.} + \text{sII} + C_1$ equilibrium [5,6], volumetric results of Ref. [6] gave $X_{\text{sII}} = 0.32(2)$ and $X_{C_1} = 0.10(2)$ near this point and along the $\text{sII} \leftrightarrow C_1$ line at temperatures down to -22°C .

The $\text{sII} \leftrightarrow C_1$ 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 $\text{sII} \leftrightarrow C_1$ transformation could play a key role in their evolution.

To directly determine the hydrogen content of the C_1 hydrate, we have recently synthesized H_2O – H_2 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_1 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_1 phase. Assuming that there was no hydrogen in the ice-VI phase, hot extraction gave $X_{C_1} \approx 1/6$ for the C_1 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 $\text{sII} \leftrightarrow C_1$ transformation (the synthesis conditions are shown by the open rhombs in Fig. 1) and quenched to the N_2 temperature. Quite unexpectedly, we produced a new hydrate

* Corresponding author at: Institute of Solid State Physics RAS, Laboratory of High Pressure Physics, Institutskaya 2, 142432 Chernogolovka, Moscow District, Russia. Fax: +74 965 249 701.

E-mail address: efimchen@issp.ac.ru (V.S. Efimchenko).

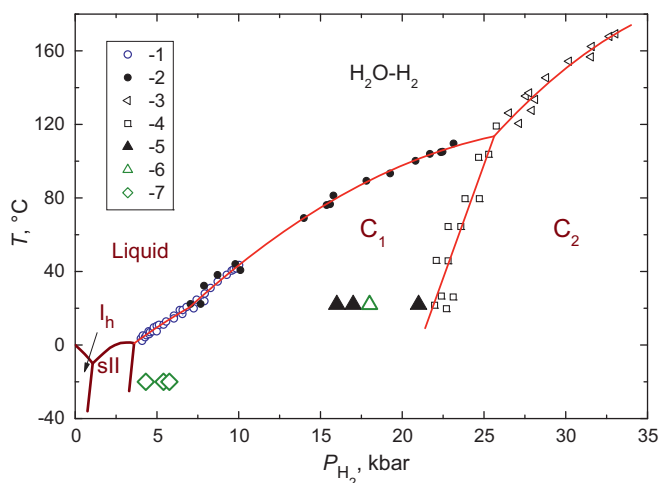


Fig. 1. T - P diagram of phase transitions in the H_2O - H_2 system with the H_2 gas taken in access. The thick solid curves at hydrogen pressures below 3.6 kbar show the melting lines of the I_h and sII phases determined by DTA [5] and later, more precisely by volumetric measurements [3], and also the lines of the $\text{I}_h \leftrightarrow \text{sII}$ [3,5] and $\text{sII} \leftrightarrow \text{C}_1$ (?) [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 $\text{C}_1 \rightarrow \text{C}_2$ transition by optical microscopy [1]. Solid triangles 5 indicate the points of the *in situ* X-ray identification of the C_1 phase [1]. Open triangle 6 indicates the synthesis conditions of the quenched C_1 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_0 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_0 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 ± 0.5 kbar, the temperature $\pm 3^\circ\text{C}$. 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 high-pressure 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 C_1 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_2O - H_2 samples thus produced were stored in liquid N_2 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.

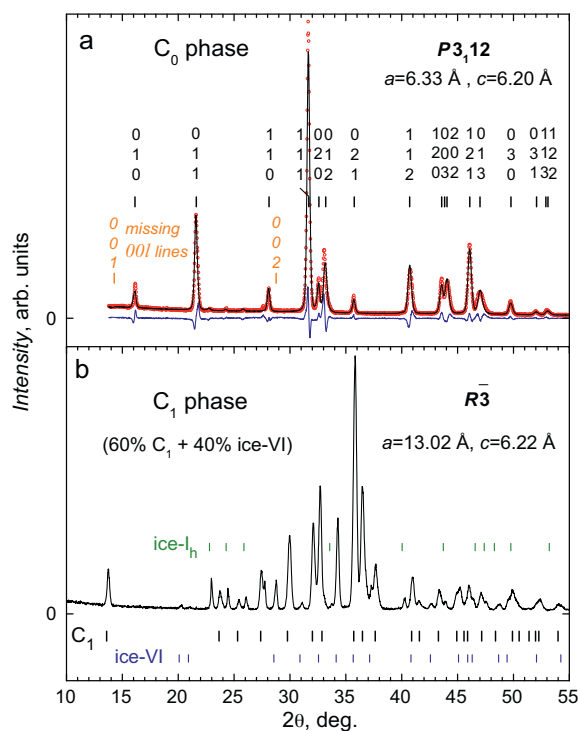


Fig. 2. X-ray diffraction patterns of H_2O - H_2 samples measured at ambient pressure and $T=80\text{ K}$ using $\text{Cu K}\alpha$ radiation. (a) The C_0 sample from the present work; the upper curve is the profile fit to the experimental pattern (open circles) and the lower curve shows the difference between this pattern and the fit (see text); (b) the C_1 sample (a mixture of 60 vol.% C_1 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_h 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 ± 0.03 kbar, the temperature $\pm 0.5^\circ\text{C}$, the volume $\pm 1\text{ mm}^3$. The procedure applied to convert the starting powder of ice- I_h 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_1 sample from Ref. [7] (b). The C_1 sample was composed of a mixture of approximately equal amounts of the C_1 phase and high-pressure ice-VI, and was also contaminated with ice- I_h 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_1 phase or ice-VI. The ice- I_h impurity manifested itself by three weak lines at $2\theta=22.8$, 24.3 and 25.9° . The sample holder gave a weak line at $2\theta=27.6^\circ$. All other lines in Fig. 2a can be indexed to a hexagonal unit cell with $a=6.33\text{ Å}$ and $c=6.20\text{ Å}$. The $(00l)$ lines with $l=1, 2$ and 4 are absent that implies the reflection condition $l=3n$, 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 $\pm 0.01\text{ Å}$. The line intensities also varied from sample to sample, so the crys-

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: $P3_1$ and $P3_2$; $P3_121$ and $P3_221$; $P3_112$ and $P3_212$. 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, $P3_1$ and $P3_112$ and $P3_121$. We started modelling the structure of the C_0 phase using the more symmetrical $P3_112$ and $P3_121$ groups. The $P3_112$ group provided a significantly better agreement with the experimental data than the $P3_121$ group, so the $P3_121$ group was ruled out. Using the $P3_1$ 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 $P3_112$.

The proposed description of the oxygen sublattice in the space group $P3_112$ allowed the most satisfactory fit to the line intensities for all three studied C_0 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_0 phase. These are the $3a_1$ 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 $3a_2$ oxygen sites and one can expect that these $3a_2$ sites serve as stoppers transforming the channels into the chains of voids. If every such void is occupied with one H_2 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_0 phase, 7.5 atoms/unit cell, corresponds to a density of about 1 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_0 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_0 structure and could make a starting point for its future refinements.

Fig. 3 demonstrates a significant difference in the thermal stability of the C_0 and C_1 phases in vacuum. If heated at 25°C/min , the C_1 phase starts evolving hydrogen at $\approx 140\text{ K}$ and completely decomposes at $\approx 200\text{ K}$. The hydrogen release from the C_0 phase begins immediately on heating above 77 K and completes at $\approx 170\text{ K}$. The maximum amount of hydrogen evolved from the C_0 samples reached $X_{C_0}=0.13$. However, in view of the instability of the samples at a nearly N_2 temperature, the equilibrium hydrogen content of the C_0 phase could be higher under the synthesis conditions ($P_{H_2}\approx 5\text{ kbar}$ and $T=-20^\circ\text{C}$). In particular, it could reach $X_{C_0}=0.2$ corresponding to the complete H_2 filling of voids in the proposed $P3_112$ 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_c .

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

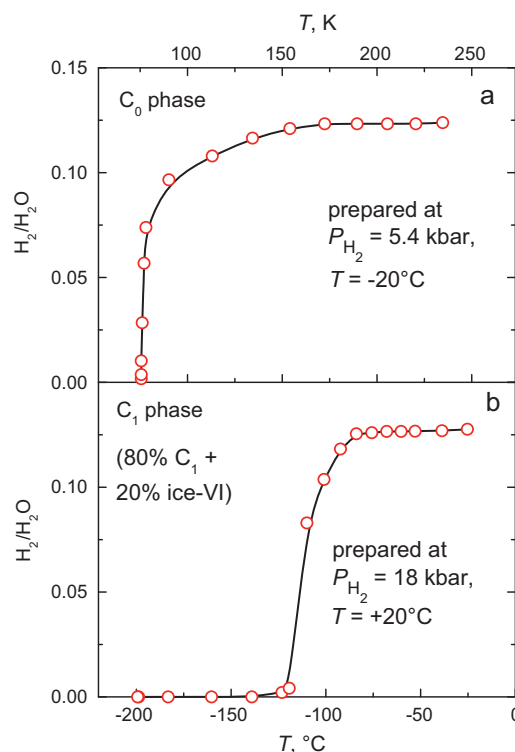


Fig. 3. Hydrogen release from H_2O – H_2 samples in the course of heating in a pre-evacuated volume at a rate of 25°C/min . (a) The C_0 sample from the present work; (b) the C_1 sample (a mixture of 80 vol.% C_1 and 20 vol.% ice-VI) from Ref. [7]. Both samples were quenched to the liquid nitrogen temperature 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_1 phase was formed at $\approx 5\text{ kbar}$ and -20°C and then transformed to the C_0 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_1 phase in the samples prepared at a higher pressure of 18 kbar and $+20^\circ\text{C}$ [7], therefore no $C_1 \rightarrow C_0$ transformation could occur at liquid N_2 temperature and lower pressures. Secondly, the diffraction patterns of the C_0 samples showed no traces of the C_1 phase, while the complete $C_1 \rightarrow C_0$ transformation in the course of the rapid cooling to the liquid N_2 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_1 phase is actually ice-II filled with H_2 molecules weakly interacting with the H_2O network [1]. Consequently, even if the C_1 phase lost some hydrogen at decreasing hydrogen pressure, its H_2O 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_0 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_2O – H_2 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

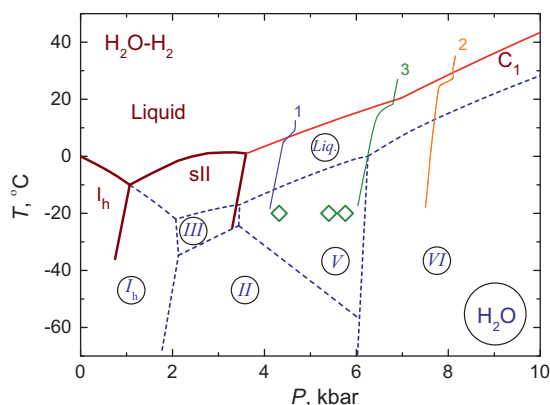


Fig. 4. T - P diagram of phase equilibria in the H_2O - H_2 system (thick solid lines) superimposed onto the diagram of H_2O [11] (dashed lines; phase fields are labelled with the encircled symbols). The thin solid curves represent isochors in the H_2O - H_2 system measured at increasing temperature: 1 – Ref. [6]; 2 – Ref. [7]; 3 – present work (see Fig. 5). Open rhombs show the synthesis conditions of the C_0 samples quenched and studied in the present work (same as in Fig. 1).

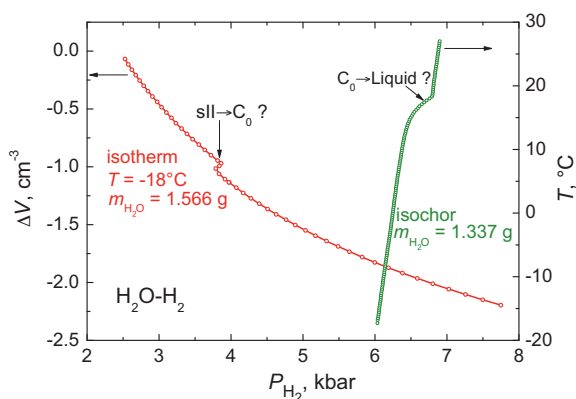


Fig. 5. Variation of volume of the H_2O - H_2 system at -18°C and increasing hydrogen pressure (the isotherm, left scale) and variation of pressure at constant volume on heating at a rate of $0.1^\circ\text{C}/\text{min}$ (the isochor, right scale).

20 min in the interval of the phase transition at $P_{\text{H}_2} \approx 3.8$ 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 $P_{\text{H}_2} \approx 3.8$ kbar attributable to a phase transformation. This can only be the $\text{sll} \rightarrow \text{C}_0$ transformation and not $\text{sll} \rightarrow \text{C}_1$ as considered earlier [6]. As seen from Fig. 4, the isochors constructed at pressures from ≈ 4.5 to ≈ 7.5 kbar and $T \geq -18^\circ\text{C}$ only have steps near the melting curve. These suggest that the C_0 phase is formed from the sll phase and does not transform to the C_1 phase at hydrogen pressures up to 7.5 kbar and temperatures from -18°C to the melting curve. Correspondingly, the triple point at 3.6(1) kbar and $+1(1)^\circ\text{C}$, which was earlier considered to be the point of the $\text{Liq.} + \text{sll} + \text{C}_1$ equilibrium [5,6], is the invariant $\text{Liq.} + \text{sll} + \text{C}_0$ point. The line radiating downwards from this point in the T - P diagram of the H_2O - H_2 system (Figs. 1 and 4) is the equilibrium line of the reversible $\text{sll} \leftrightarrow \text{C}_0$ transformation.

Results of the present paper show that the C_0 phase is stable below the melting curve, which ascends to $\approx 25^\circ\text{C}$ at 7.5 kbar. According to [1], the C_1 phase is stable at temperatures above $22(3)^\circ\text{C}$ and pressures above 7.5 kbar. The line of the $\text{C}_0 \leftrightarrow \text{C}_1$ 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 ≈ 7 kbar and $\approx 20^\circ\text{C}$ (see thin solid curves in Figs. 1 and 4). One can speculate that this is the triple point of the $\text{Liq.} + \text{C}_0 + \text{C}_1$ equilibrium. (Note that the suggested location of the triple point at a pressure of 7 kbar does not contradict the observed absence of the $\text{C}_0 \rightarrow \text{C}_1$ 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_0 is discovered in the H_2O - H_2 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_0 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_0 hydrate is stable in the T - P region below 8 kbar, which was earlier considered as part of the stability field of the C_1 hydrate. Constructing the high-pressure boundary of the C_0 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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