



## Structural Investigations of Argon Hydrates at Pressures up to 10 kbar

A.YU. MANAKOV<sup>1,\*</sup>, V.I. VORONIN<sup>2</sup>, A.V. KURNOSOV<sup>1</sup>, A.E. TEPLYKH<sup>2</sup>, V.YU. KOMAROV<sup>1</sup>  
and YU.A. DYADIN<sup>†</sup>

<sup>1</sup>Institute of Inorganic Chemistry SD RAS, Ac. Lavrentiev av. 3, Novosibirsk, 630090, Russia; <sup>2</sup>Institute of Metal Physics UD RAS, S.Kovalevskoy st. 18, Yekaterenburg, 620219, Russia

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### Abstract

Neutron diffraction patterns of three argon hydrates which exist at the pressures up to 10 kbar has been studied; Rietveld refinement of their structures has been done. The phase which is stable from 1 bar to 4.6 kbar appears to be typical cubic structure II gas hydrate with variable degree of filling of the large cavities. Stoichiometry of this compound under high-pressure conditions has been determined for the first time and appears to be Ar·4.5H<sub>2</sub>O and Ar·4H<sub>2</sub>O at 3.4 and 4.3 kbar, respectively. Gas hydrate existing in the pressure range of 4.6–7.7 kbar has a hexagonal structure (hexagonal structure III, so-called structure H). Refinement of the structure has shown that the best agreement between calculated and experimental pattern can be reached in the case of accommodation of five (!) argon atoms in the large cavity. Indexing of the neutron diffraction pattern of the hydrate stable in the 7.7–9.5 kbar range leads to the primitive tetragonal unit cell with parameters  $a = 6.342 \text{ \AA}$ ,  $c = 10.610 \text{ \AA}$  at 9.2 kbar, which does not correspond to any known type of gas hydrates. The water framework of this structure was found by idealizing the structure of pinacol semiclathrate hydrate. This hydrate belongs to a new, earlier unknown, tetragonal structural type of gas hydrates. It contains only one type of polyhedral cavities with 14 faces. This type of polyhedrons are space-filling; two argon atoms occupy each cavity. This structure gives the first example of the gas hydrate water framework which contains only one type of polyhedral cavities.

**Abbreviations:** CS-I – cubic structure I; CS-II – cubic structure II; HS-III (or structure H) – hexagonal structure III; TS-IV – tetragonal structure IV

### Introduction

Gas hydrates form one of the classes of inclusion compounds in which the molecules of a gas or a readily volatile liquid are located in the cavities of a polyhedral framework composed of water molecules; the guest–host interaction is of purely van-der-Waals type. A reason for permanent interest in these compounds during the recent 15 years is the discovery of enormous deposits of gas hydrates in nature (the Earth's interior and ocean floor contain about  $2 \times 10^{16} \text{ m}^3$  of natural gas in the form of gas hydrate [1]). Investigations of recent years show that the gas hydrate constituent of natural ecosystems can have a substantial effect on a number of global processes (for example, climate changes). Probable existence of gas hydrates on some celestial bodies is of interest, too.

About half a century has passed since the time when Shtakelberg, Pauling and Claussen discovered two structures of gas hydrates: cubic structures I and II [2–4]. Not long ago, the third type of polyhedral gas hydrate structures was discovered: hexagonal structure III, which occurs in the

case of double hydrates [5, 6]. The overwhelming majority of gas hydrates known at present, which exist under moderate (up to several hundred atmospheres) pressure, belong to these three structural types [7, 8]. The latest structural investigations of gas hydrates have increased the number of known structural types of these compounds existing at atmospheric pressure. The authors of [9] solved principally a new hexagonal structure of dimethyl ether hydrate. It was demonstrated that one of the hydrates of bromine relates to the tetragonal structure which previously was observed only in the hydrates of tetraalkylammonium salts [10]. Finally, the broadening of pressure range within which structural investigations were performed has immediately promoted the discovery of new structures of gas hydrates. Known structural types of gas hydrates are discussed in detail in [7, 8], we will not consider them here.

Due to the friability of packing for many gas hydrates and due to the low bonding energy of water molecules comprising the host lattice (hydrogen bonds), the systems in which gas hydrates are formed are very sensitive to variations of pressure. However, because of substantial experimental difficulties, systematic investigation of gas hydrates at high pressure started only in the recent years. A number of in-

\* Author for correspondence.

† Deceased.

vestigations of the phase diagrams of gas hydrate forming systems (including water – inert gases, hydrogen, methane, ethane, propane, tetrahydrofuran, etc.) at pressures up to 15 kbar [for example, 11–16] indicated that in nearly all the investigated systems an increase in pressure causes subsequent changes of hydrate phases connected with tightening of their packing. The authors of [17, 18] investigated the structures of compounds formed in hydrogen – water and helium – water systems. It turned out that gas hydrate phases in these systems under high pressure are formed due to the inclusion of guest molecules into the frameworks of ices II and Ic. The analysis of phase diagrams at high pressures in inert gas (hydrogen) – water system (taking into account the results of [17, 18]) has led the authors of [14] to the hypothesis concerning the formation of ice-like high-pressure hydrates also in the systems composed of neon, argon, or krypton – water. Ice-like hydrate was detected experimentally for the first time in the methane–water system (for which only the formation of polyhedral hydrates was previously considered to be possible) [19–22]; subsequent investigations confirmed the existence of such a hydrate also in the argon system (hydrate  $h_3$  in Figure 3 [23]).

A very important result concerning the possibility for large cavities of polyhedral gas hydrate structures to be filled with several guest molecules has been obtained in [24, 25] for a nitrogen – water system. In those works, the investigation was performed at a pressure up to 3 kbar, so high-pressure phases had not been investigated.

In the present study, we report the results of neutron diffraction investigation of gas hydrates formed in argon – heavy water system at pressure up to 10 kbar, and the phase diagram of argon – heavy water system. Intermediate results have been published as short communications [26, 27].

## Experimental

The investigation was performed with the IVV-2M research reactor (Ekaterinburg) [28] at  $\lambda = 2.4236 \text{ \AA}$ , some powder neutron diffraction patterns were investigated with a high-resolution diffractometer at  $\lambda = 1.51296 \text{ \AA}$ . Neutron diffraction patterns were recorded in Debye–Scherer geometry, the profile of diffraction peaks was approximated by Gaussian. The structure was refined using the “FullProf” software [29].

Investigations were performed in a high-pressure chamber of the piston – cylinder type, made of titanium-zirconium alloy which gives no reflections in the neutron diffraction patterns. The working pressure in the chamber is up to 10 kbar; pressure is measured according to the strain applied to the piston. The error in the pressure measurements may be estimated as  $\pm 0.2$  kbar. The volume of the sample on which the neutrons diffract is  $1.6 \text{ cm}^3$ . The chamber has been described in detail in [30]. Heavy water (not less than 99.7%  $D_2O$ ) and argon (purity: 99.9%) were used in the investigation. To obtain a hydrate sample, we washed the working volume of the device with argon at the liquid nitrogen temperature; after that, finely crushed ice ( $D_2O$ ) was loaded into the apparatus and an excess of liquid argon was poured in. After that, the chamber was closed and kept for 1

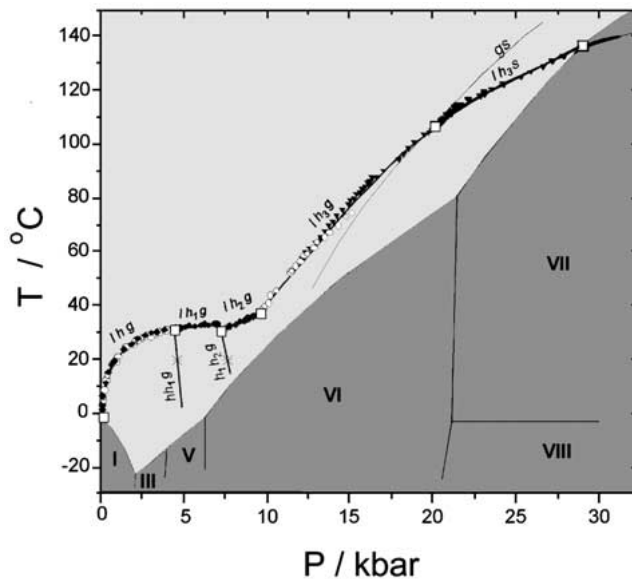


Figure 1. Phase diagram of the argon – water system. Solid diamonds – data Ref. [32]; open rings – data Ref. [12]; solid triangles – data Ref. [33]; stars – data of this work. Open squares – quadruple points,  $h$ ,  $h_1$ ,  $h_2$ ,  $h_3$  – different hydrate phases;  $I$  – water rich liquid phase;  $g$  – fluid phase;  $2$  – solid argon. Roman digits denote fields of stability of the respective ices.

hour at a temperature below  $-25 \text{ }^\circ\text{C}$  for the sufficient number of nuclei of the hydrate phase to be formed in the reaction of ice with gaseous argon (pressure in the chamber was not controlled during this period but it can be estimated as 500 bar). Then the pressure in the chamber was raised. The equilibrium was establishing in the system within several days, which was expressed as a spontaneous decrease in pressure in the apparatus. Neutron diffraction patterns were recorded at room temperature (about  $20 \text{ }^\circ\text{C}$ ). In processing the experimental data, we did not notice any preferential orientation of crystals in the samples. The differential thermal analysis procedure has been described in detail in [31].

## Results

### Phase diagram of the argon – water system

The phase diagram of the argon–water system has been studied thoroughly (Figure 1). In the early work [32] the decomposition curve of the argon hydrate which exists at atmospheric pressure has been studied up to pressures of 4 kbar. In Ref. [12], investigation was performed by means of differential – thermal analysis at pressure up to 15 kbar; the formation of three hydrates ( $h$ ,  $h_2$ ,  $h_3$ ) was established reliably, though it was noted that a phase transition is very probable at a pressure about 4.5 kbar; one of the reasons might be the existence of one more hydrate. Subsequent investigations confirmed the existence of that phase ( $h_1$ ) and substantially broadened the range of the investigated pressures [26, 33]; no new hydrate phases were observed during these studies. So, the existence of four hydrates has been reliably stated in the investigations of phase diagram of argon – water system.

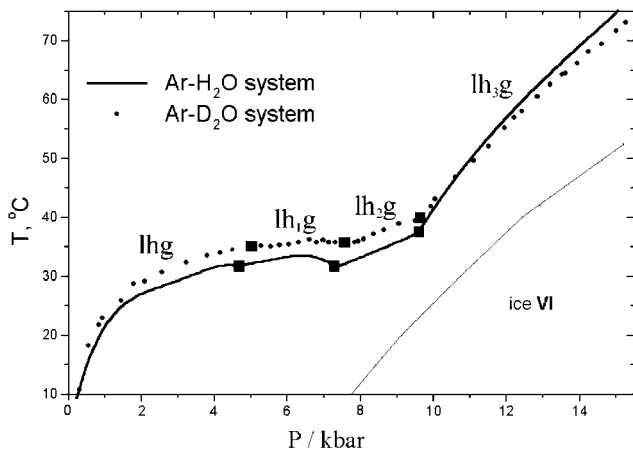


Figure 2. Decomposition lines of gas hydrates which form in Ar–H<sub>2</sub>O and Ar–D<sub>2</sub>O systems. Solid squares denote quadruple points in the respective systems.

With a smooth increase in volume of the high-pressure apparatus, in our experiments we detected pressure jumps at about 4.6 and 7.7 kbar (temperature: 20 °C), which are the evidences of phase transitions; this well agrees with the experimental phase diagram (Figure 1). The lines of hydrate decomposition in the D<sub>2</sub>O–argon system (Figure 2, our data) up to the pressure of 10 kbar go higher than in the H<sub>2</sub>O–argon system by 2–3 degrees, which corresponds to usual isotope effect in systems with light and heavy water. A sharp drop of the decomposition line before the quadruple point corresponding transformation of **h**<sub>1</sub> hydrate to **h**<sub>2</sub> hydrate in the system with D<sub>2</sub>O is much less vividly expressed than in the system with H<sub>2</sub>O. A very interesting feature of the system with heavy water is observed at pressure above 10 kbar (in the region of the existence of **h**<sub>3</sub> hydrate). The decomposition line of deuterohydrate goes lower than that for the hydrate of argon with light water. We suppose that this fact can be interpreted on the basis of the data on ice-like structure of **h**<sub>3</sub> hydrate [19, 23]. The diameter of argon atom (3.8 Å) does not allow it to be freely located in the channels of the hydrate framework, so rather substantial stretching of hydrogen bonds is necessary for introducing argon into those channels. Since the energy of O–D–O hydrogen bond is somewhat higher than that of O–H–O [34], the formation of such a hydrate in the system with heavy water is less profitable.

#### The structures of **h** and **h**<sub>1</sub> hydrates

At the moment when we started the present research, only the structure of the hydrate existing at atmospheric pressure was studied; it relates to the CS-II. Experimental neutron diffraction patterns of the argon deuterohydrates at three pressure values are shown in Figure 3. In neutron diffraction patterns of the phase which is stable within pressure range 1 bar to 4.6 kbar, all the reflections can be indexed on the basis of CS-II, which coincides with the data on the structure of argon hydrate at atmospheric pressure [7, 36]. The structure was refined at two pressure values: 3.4 and 4.3 kbar (Figure 3a, b). Starting atomic coordinates of oxygen

and deuterium atoms were taken from Ref. [37]. Unit cell parameters, atomic coordinates, occupation factors for guest atoms and background were refined with Rietveld method. Some data on the refined structures are presented in Table 1. In both cases, water lattice has no substantial differences from that known in literature [37]. The unit cell of this hydrate contains 16 pentagondodecahedral cavities (small *D*-cavities with 12 pentagonal faces) and 8 hexakaidodecahedra (large *H*-cavities with 4 hexagonal and 12 pentagonal faces). Unit cell formula of the hydrate – 8H\*16D\*136H<sub>2</sub>O. In more details this structure is discussed in [7, 8]. Lengths and angles of hydrogen bonds somewhat differ from those characteristic of the given structural type of gas hydrates at atmospheric pressure, however, they do not come out of the limits of values determined experimentally for different clathrate hydrates [34] and can be explained by the deformation of the lattice of argon hydrate under the action of pressure. Isotropic thermal parameters for oxygen and deuterium were taken close to the values for ices at similar pressure [18, 38], our attempts to refine them has not shown significant changes of these parameters. In final refinement isotropic thermal parameters *B* were fixed as 3.0 Å<sup>2</sup> for oxygen atoms and 3.5 Å<sup>2</sup> for deuterium atoms to increase the value of the data-parameters ratio (ratio of the number of the visible reflection peaks to the number of parameters of the refinement). Argon atoms accommodated in the large cavity were set as disordered in four positions, shifted from the cavity center to the centers of hexagonal faces; occupation factors of these positions was refined. With such a position of several argon atoms in the cavity, in our opinion, thermal factor for them cannot be substantially different from that for other atoms of the structure. At the final refinement, the thermal factor for argon in the large cavity was accepted to be equal to 3.0 Å<sup>2</sup> (similar to that for oxygen). With varying thermal factor (*B*) for argon within a reasonable range (2.5–6 Å<sup>2</sup>), the filling of the position was changed within several per cent. The refined mean content of argon atoms in the large cavity is shown in Table 1. Since the presence of cavities not filled with guest is not probable at such a high pressure, while more than one argon atom cannot be placed in a small cavity because of geometric considerations, we placed one argon atom per small cavity center when refining; isotropic thermal parameter for this atom was chosen in trial and error procedure. Our attempts to refine isotropic thermal parameters does not influence significantly the results of refinement (except for argon atoms in the small cavity) and in some cases made the refinement unstable; that was one more reason to fix them.

The treatment of neutron diffraction patterns of the hydrate existing in pressure range 4.6–7.7 kbar showed that all the reflections are indexed in the hexagonal system, with the unit cell parameters which corresponds to the known HS-III structural type of hydrates. Starting atomic coordinates of oxygen atoms in this structure were taken from Ref. [6]; deuterium atoms were positioned at 1/3 and 2/3 of the hydrogen bond. Rietveld refinement of the structure of this hydrate (Figure 3c) showed that its water lattice has no substantial differences from that determined for this structural

Table 1. Some refined parameters of argon hydrates

Type	CS-II	CS-II	HS-III	TS-IV
Pressure/kbar	3.4	4.3	7.6	9.2
Space group	$F d\bar{3}m$	$F d\bar{3}m$	$P 6/mmm$	$P 4_2/mnm$
Unit cell parameters/Å	$a = 17.075$ (1)	$a = 16.974$ (1)	$a = 11.979$ (1) $c = 9.870$ (1)	$a = 6.342$ (2) $c = 10.610$ (3)
Unit cell volume/Å <sup>3</sup>	4978 (1)	4890 (1)	1226.6 (2)	426.7 (3)
Unit cell formula	30.4Ar·136D <sub>2</sub> O	34Ar·136D <sub>2</sub> O	10Ar*34H <sub>2</sub> O	4Ar·12H <sub>2</sub> O
Stoichiometry	Ar·4.5(2)D <sub>2</sub> O	Ar·4.0(2)D <sub>2</sub> O	Ar·3.4(2)D <sub>2</sub> O	Ar·3H <sub>2</sub> O
Density, g/cm <sup>3</sup>	1.31 (2)	1.39 (2)	1.46 (3)	1.557 (1)
Number of argon atoms				
in large cavity	1.8 (2)	2.3 (2)	5.0 (6)	2 <sup>1</sup>
R-factor (%)	9.10	9.47	9.66	8.5
Hydrogen bond				
distances/Å	2.65–2.82	2.67–2.78	2.67–2.85	2.64–3.04
O–O–O angles/deg.	102.6–119.5	103.9–119.7	90–120	90–129.9
Shortest distances/Å				
• O–Ar	2	2	3.17	3.25
• Ar–Ar			3.7	3.5

<sup>1</sup>Only one type of cavities present in the structure.

type at atmospheric pressure [6]; the data on this structure are presented in Table 1. The structure contains three types of cavities: large  $E$ -cavity (8 hexagonal and 12 pentagonal faces), two  $D'$  small cavities (3 square, 6 pentagonal and 3 hexagonal faces) and 3 pentagondodecahedral cavities. Unit cell formula of this hydrate –  $E^*2D'^*3D^*34H_2O$ . In more details this structure is discussed in [6, 8]. The structure was refined similarly to that of CS-II. The filling of large cavity of this structure with argon was quite unexpected for us. The cavity has the maximal size among the known ones for gas hydrates; its inner volume can be represented as an ellipsoid with the axes about 10 and 7 Å. Initially, 2–3 argon atoms were assumed to be placed in it; however, in refining, the best correspondence was obtained for the model with five (!) argon atoms. Their location in the cavity corresponds to the vertices of a trigonal bipyramid in which three argon atoms are located in the equatorial plane of the cavity (there are two equivalent positions for each of these atoms, which corresponds to disordering of three atoms around a sixth-order axis, Figure 4). On the basis of results of refinement, we concluded that the filling extent is 50% for each of the six argon positions in the equatorial plane of large cavity and 100% for the remaining two axial positions. So, five argon atoms are placed in each large cavity of the structure. Distances between argon atoms in the large cavity and between argon atoms and the atoms of framework do not differ substantially from expected from the van-der-Waals radii. Similarly to the case of CS-II hydrates, small cavities are filled with one argon atom. Significant errors in the positions of some atoms which were obtained in the refinement procedure may be explained by small distortions of the real structure from the chosen model (Prof. J. Tse, private communication). Unfortunately, the refinement of this structure in lower symmetry leads to low value of the data-parameters ratio that make the procedure nonsensical.

### The structure of $h_2$ hydrate

The neutron diffraction patterns of a hydrate which is stable at pressure of 7.7–9.5 kbar (Figure 5) could not be described by the known structures of clathrate hydrates. Indexing of the neutron diffraction patterns showed that this hydrate can be described as a tetragonal one with unit cell parameters  $a = 6.342$  Å,  $c = 10.610$  Å at 9.2 kbar and room temperature. We did not succeed in solving the hydrate structure by the direct method, but a search for an independent model suitable in symmetry and unit cell parameters was successful. The water framework of the found structure was obtained by idealization of the structure of semi-clathrate hydrate of pinacol [39]. By refining the coordinates of all atoms and unit cell parameters, we achieved rather good agreement between the neutron diffraction patterns calculated with the theoretical model and the patterns obtained experimentally (R-factor: 8.5%, Figure 5). To maintain the system of notations suggested in [35] we will refer to this structure as tetragonal structure IV (TS-IV). The refined coordinates of basis atoms are shown in Table 2. Two argon atoms occupy each cavity. Partial occupation of the cavities by argon atoms at the pressures at which this hydrate is stable is not probable; in the refinement 100% occupation of all positions was accepted. A unit cell contains 12 water molecules ( $Z = 4$ ), the stoichiometry of hydrate is  $Ar^*3D_2O$ . Some data concerning this structure are shown in Table 1. Taking into account measurement errors in our experimental data, scattering of the parameters characterizing water lattice can be considered to be close to that obtained in investigating high-pressure ice modifications. Refined isotropic thermal factors turned out to be close to those obtained under the corresponding  $P, T$  – conditions for ices and helium hydrates on the basis of water framework of ice II [18, 38]; they were fixed for the final refinement of the structure. A fragment of the structure is shown in Figure 6a. The water framework

Table 2. Atomic coordinates of argon hydrates

Atom	x	y	z	$B_{\text{iso}}/\text{\AA}^2$	Occupancy
CS-II hydrate at 3.4 kbar					
O1	0.125	0.125	0.125	3.0	0.04166
O2	0.220 (1)	0.220 (1)	0.220 (1)	3.0	0.16666
O3	0.180 (9)	0.180 (9)	0.370 (1)	3.0	0.5
D1	0.181 (1)	0.181 (1)	0.181 (1)	3.5	0.08333
D2	0.161 (1)	0.161 (1)	0.161 (1)	3.5	0.08333
D3	0.204 (1)	0.204 (1)	0.273 (2)	3.5	0.25
D4	0.194 (2)	0.194 (2)	0.316 (2)	3.5	0.25
D5	0.141 (1)	0.141 (1)	0.377 (1)	3.5	0.25
D6	0.164 (2)	0.231 (2)	0.391 (2)	3.5	0.5
Ar1 ( <i>D</i> -cavity)	0.000	0.000	0.000	7.0	0.08333
Ar2 ( <i>H</i> -cavity)	0.418	0.418	0.418	3.5	0.073 (9)
HS-III hydrate at 7.6 kbar					
O1	0.792 (9)	0.585 (3)	0.269 (3)	3.0	0.5
O2	0.3333	0.6667	0.363 (6)	3.0	0.16667
O3	0.384 (2)	0.00000	0.135 (3)	3.0	0.5
O4	0.863 (9)	0.725 (3)	0.5000	3.0	0.25
D11	0.752 (9)	0.505 (3)	0.682 (5)	3.5	0.25
D12	0.709 (9)	0.418 (3)	0.666 (5)	3.5	0.25
D21	0.859 (3)	0.271 (3)	0.211 (3)	3.5	0.5
D22	0.926 (3)	0.328 (3)	0.186 (4)	3.5	0.5
D31	0.826 (9)	0.652 (5)	0.650 (5)	3.5	0.25
D32	0.832 (9)	0.665 (4)	0.583 (4)	3.5	0.25
D41	0.3333	0.6667	0.460 (9)	3.5	0.08333
D51	0.529 (3)	0.00000	0.845 (3)	3.5	0.25
D71	0.953 (3)	0.778 (4)	0.5000	3.5	0.25
D81	0.374 (3)	0.0000	0.035 (5)	3.5	0.25
Ar11 ( <i>E</i> -cavity)	0.00000	0.0000	0.297 (15)	3.0	0.083 (16)
Ar12 ( <i>E</i> -cavity)	0.218 (15)	0.109 (20)	0.00000	3.0	0.125 (22)
Ar3 ( <i>D'</i> -cavity)	0.6667	0.3333	0.00000	7.0	0.08333
Ar4 ( <i>D</i> -cavity)	0.5000	0.5000	0.50000	7.0	0.125
TS-IV hydrate at 9.2 kbar					
O1	0	0.5	0.25	2.0	0.25
O2	-0.147(3)	0.147(3)	0.643(3)	2.0	0.5
D1	-0.041(5)	0.615(3)	0.290(2)	2.5	0.5
D2	0.109(4)	0.281(3)	0.659(2)	2.5	0.5
D3	0.175(2)	0.175(2)	0.541(2)	2.5	0.25
D4	0.944(3)	0.944(3)	0.374(2)	2.5	0.25
Ar	0.181(5)	0.181(5)	0	2.0	0.25(1)

is composed of one type of polyhedral cavities filling the space (Figure 6b), the so-called Williams' diheptahedrons [40] containing two quadrangle faces, four hexagonal faces and eight pentagonal faces ( $4^25^86^4$ ). Vertices of polyhedrons are oxygen atoms, while the edges are hydrogen bonds. It is interesting to note that the shape of the cavity obtained by us corresponds to one of polyhedrons which filling the space and has the smallest ratio of surface area to volume. In general, the framework can be considered as two identical layers of polyhedrons turned over each other by  $90^\circ$ . Inside a layer, polyhedrons verge on each other over the tetragonal and hexagonal faces, while the layers verge on each other over pentagonal faces. The possibility for the hydrates with such

a topology of polyhedral framework to exist was considered in [40].

The occurrence of tetragonal faces leads to some strain in the structure (i.e., to some loss of energy), since the angle between hydrogen bonds ( $90^\circ$ ) differs rather substantially from the valence angle ( $105^\circ$ ). A very efficient packing of atoms in the crystal structure of this hydrate evidently compensates this loss, which leads to the realization of this structure under increased pressure. What is more, one cavity has only two tetragonal faces, while in the case of another polyhedron filling the space, namely, truncated octahedron, there are six tetragonal faces per cavity. Shortening of the distance between the argon atoms in a cavity, in comparison with the sum of van-der-Waals radii, is very substantial;

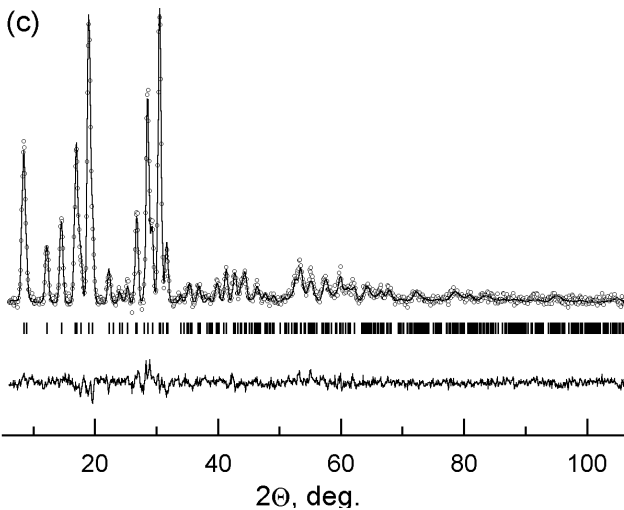
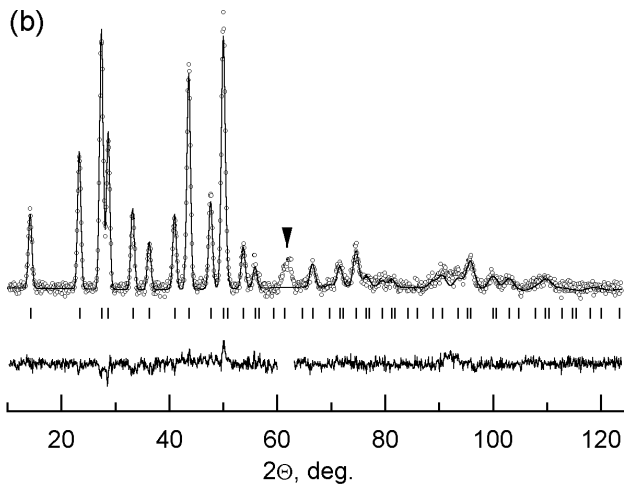
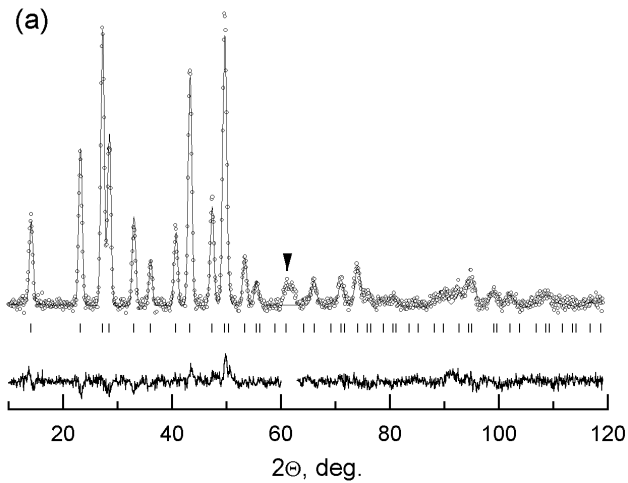


Figure 3. Experimental neutron diffraction pattern of argon hydrates (data points) and the profile obtained upon structure refinement (solid line). (a) CS-II hydrate at 3.4 kbar ( $\lambda = 2.4236 \text{ \AA}$ ); (b) CS-II hydrate at 4.3 kbar ( $\lambda = 2.4236 \text{ \AA}$ ); (c) HS-III hydrate at 7.6 kbar ( $\lambda = 1.51296 \text{ \AA}$ ). Tick marks show the positions of allowed reflections. A differences curve is plotted beneath. The marked reflection arose from a part of the high-pressure apparatus and was not introduced into the refinement.

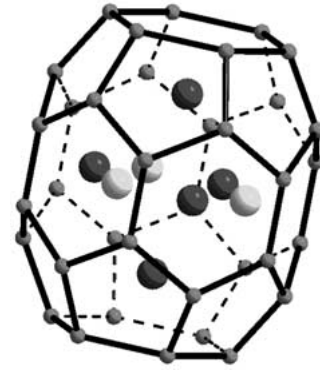


Figure 4. Accommodation of 5 argon atoms in the large *E*-cavity of HS-III. For explanations see the text.

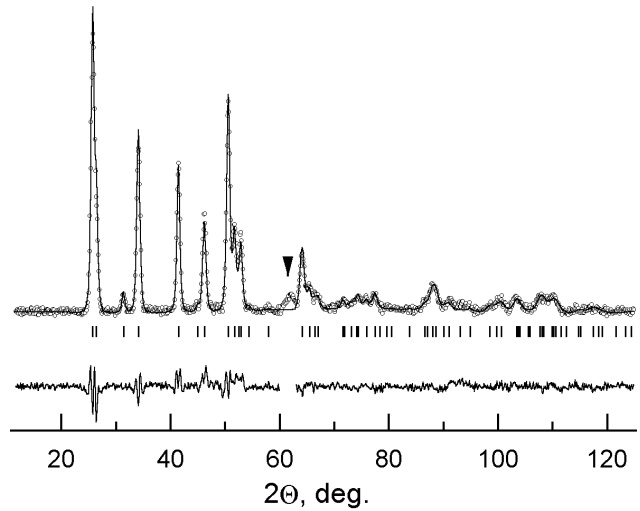


Figure 5. Experimental neutron diffraction pattern of tetragonal argon hydrate at 9.2 kbar (data points;  $\lambda = 2.4236 \text{ \AA}$ ) and the profile obtained upon structure refinement (solid line). Tick marks show the positions of allowed reflections. A differences curve is plotted beneath. The marked reflection arose from a part of the high-pressure apparatus and was not introduced into the refinement.

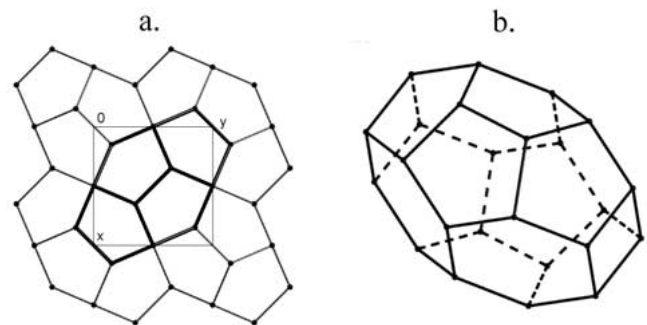


Figure 6. (a) Packing of tetradecahedral cavities in the tetragonal structure of argon hydrate. The center of the cavity outlined with thick lines is located at the point with the coordinate  $z = 0.5$ ; for the centers of the remaining cavities,  $z = 0$ . (b) A general view of the tetradecahedral cavity in the new structure.

however, this is quite reasonable, taking into account the known experimental data on compressibility of pure argon [41].

## Discussion

All the structures considered above can be represented as layered ones; the CS-II and HS-III are composed of the layers of one type (Figure 7, [35]) with layers alternation of ABC and AAA, respectively. These hexagonal layers occur also in other gas hydrate structures, which can undoubtedly be explained by the profitableness of the formation of pentagondodecahedron from water molecules (since the distortions of hydrogen bonds connected with this process are minimal). The transition of hydrate from CS-II to HS-III is not accompanied by any substantial tightening of packing; this is seen from the phase diagram (almost the same slope of the decomposition lines of argon hydrates  $h$  and  $h_1$  at the quadruple point) and is confirmed by structural data. In addition, the presence of tetragonal faces in HS-III makes the framework of this structure less profitable from the viewpoint of energy, in comparison with the framework of CS-II. Taking into account the above considerations, a sole explanation of this transition is the necessity for a substantial deformation of the water framework of CS-II when more than 2 argon atoms are introduced into the large cavity of the structure (as follows from the refined stoichiometry). By the shift of layers, corresponding to the transformation of CS-II into HS-III, two large  $H$ -cavities of the CS-II are united into one  $E$ -cavity of the HS-III, which can be filled with five argon atoms without any distortion of the water framework, which makes the formation of a structure with large cavities more profitable. Further tightening of the packing within the approach of the classical polyhedral structures of gas hydrates is impossible in the given system, because a very efficient packing of argon atoms in the large cavity is already achieved in the HS-III, while the efficiency of filling the small cavity with one argon atom is low (van-der-Waals' diameter of argon is  $3.8 \text{ \AA}$ , the free diameter of a small cavity is about  $5.2 \text{ \AA}$ ). The new tetragonal structure discovered by us shows one of the ways of adaptation to an increase in pressure in the systems in which gas hydrates are formed.

The tetragonal structure can also be described as an alternation of the layers composed of water pentagons (ABAB, B layer is rotated by  $90^\circ$ , with respect to the A layer; Figure 6a shows the binding of water molecules in the layer); several examples of such layers in semi-clathrate hydrates are known [34]. High density of packing is achieved in the structure (absence of vacant cavities, good fit of the shape and size of guest in the cavity); the energy-profitable pentagon composition of the layer is conserved to a substantial extent. At the same time, the structure conserves the features of a layered one: the length of one of the interlayer hydrogen bonds is noticeably increased. In general, this structure can be considered as an intermediate one between the classical polyhedral gas hydrate structures and the tightest ice-like ones.

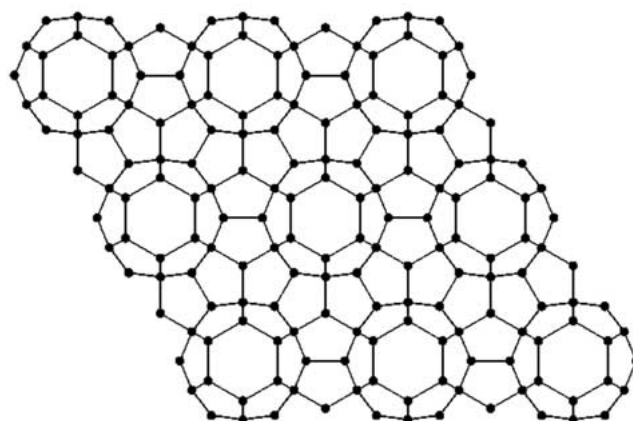


Figure 7. Hexagonal layer constructed from pentagondodecahedral cavities.

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