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A New Gas Hydrate Structure

A. V. Kurnosov*, A. Yu. Manakov*, V. Yu. Komarov*,
V. I. Voronin**, A. E. Teplykh**, and Yu. A. Dyadin*

Two gas hydrate structures—cubic structures I and II (CS-I and CS-II, respectively)—were discovered by von Stackelberg, Pauling, and Claussen about half a century ago [1–3]. Recently, a third type of gas hydrate structure, hexagonal structure III (HS-III) found in double hydrates, has been reported [4]. The vast majority of gas hydrates available at moderate pressures (up to several hundreds of atmospheres) belong to these three structural types [5]. Therefore, the structures of gas hydrates ("ideal clathrates" in which the guest molecule does not participate in the formation of the hydrate framework) noticeably rank below the structures of clathrate hydrates in diversity; more than ten such structures can be counted [6]. Studies of phase diagrams of the systems in which gas hydrates exist at high pressures have shown that several hydrate phases can form in the same guest–water system [6, 7]. Available structural information on high-pressure gas hydrate phases is scarce. To the best of our knowledge, the list of relevant publications include only eight entries; besides our previous paper [8], only one of these papers reports on the discovery of a new type of gas hydrate structure [9]. In the cited studies, these structures were not characterized by crystallographic data; only unit cell parameters were reported. In this paper, we describe a new (fourth) structural type of gas hydrate characterized by us in the course of neutron diffraction studies of high-pressure gas hydrate phases in the argon–water and tetrahydrofuran–water systems.

Our neutron diffraction study of the first three (in order of increasing pressure) hydrates in the argon–heavy water system [8] showed that the third hydrate (a total of four hydrates were found in this system), which is stable at pressures of 7.7–9.6 kbar (this range corresponds to the positions of quadruple points in the phase diagram of the argon–H_2O system), belongs to the tetragonal structural type, previously unknown among gas hydrates. Figure 1 shows the corresponding neutron powder diffraction pattern. The experimental procedure

* Institute of Inorganic Chemistry, Siberian Division,
  Russian Academy of Sciences,
  pr. Akademika Lavrent'eva 3, Novosibirsk, 630090 Russia
** Institute of Metal Physics, Ural Division,
  Russian Academy of Sciences, ul. S. Kovalevskoi 18,
  Yekaterinburg, 620219 Russia

was described in [8]. The radiation wavelength was $\lambda = 2.4236$ Å. We failed to solve the structure of this hydrate by direct methods; however, we found an independent model that was suited to the symmetry and unit cell parameters of this hydrate. The water framework of this structure was found by idealizing the structure of pinacol semiclathrate hydrate [10]. The structure was refined with the FullProf program [11]. The refined unit cell parameters of argon hydrate were as follows: $a = 6.342(2)$ Å, $c = 10.610(3)$ Å ($P = 9.2$ kbar, room temperature), space group $P4_2/mnm$ (the tentative space group $P4_22_12$ reported in [8] is a subgroup of this group). The unit cell of the framework contains 12 wate molecules forming two cavities. The refined isotropic thermal factors appeared to be similar to those found under corresponding P,T-conditions for ices and helium hydrates based on the ice II lattice [12, 13]. In the course of refinement of all atomic coordinates and unit cell parameters, we obtained the calculated neutron diffraction pattern from a theoretical model that satisfactorily fitted the experimental pattern ($R = 7.9\%$). The refined coordinates of basis atoms are listed in the table.

Figure 2, *1* shows a fragment of the structure. The water framework consists of identical space-filling polyhedral cavities (Fig. 2, *2*), so-called Williams' tetradecahedra [14], containing two tetragonal faces, four hexagonal faces, and eight pentagonal faces ($4^2 5^8 6^4$). The vertices of polyhedra are oxygen atoms, and their edges are hydrogen bonds. Note that the shape of this cavity corresponds to one of the space-filling polyhedra with the smallest surface area-to-volume ratio. As a whole, the framework can be visualized as two identical sheets of polyhedra rotated through 90° with respect to each other. In a sheet, the polyhedra share tetragonal and hexagonal faces, and polyhedra from neighboring sheets share pentagonal faces. Each cavity accommodates two argon atoms. The unit cell contains 12 water molecules per two cavities; thus, the stoichiometric ratio for argon as a guest is three water molecules per argon atom.

The presence of tetragonal faces results in some stress in the structure (i.e., in some energy loss), because the angle between hydrogen bonds (90°) noticeably differs from the tetrahedral angle (109.5°). The high packing coefficient ($k_p \sim 0.77$) evidently com-
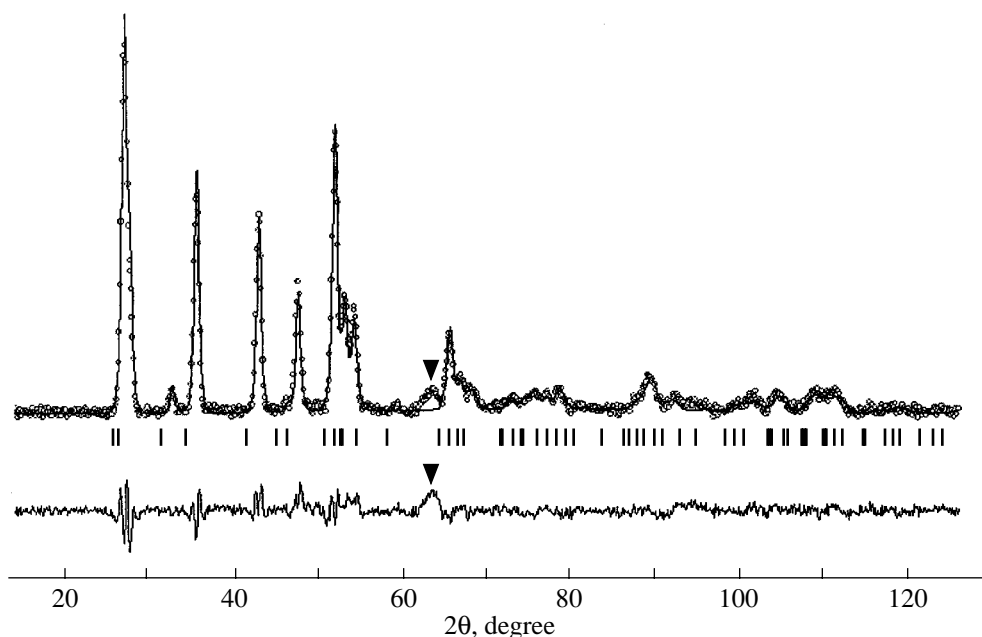
Fig. 1. Experimental neutron powder diffraction pattern of argon hydrate (data points) and the profile obtained upon structure refinement (solid line). Tick marks show the positions of allowed reflections. A differences curve (observed minus calculated) is plotted beneath. The marked reflection arose form a part of the high-pressure setup and was not introduced into the refinement.

(*1*)   (*2*)
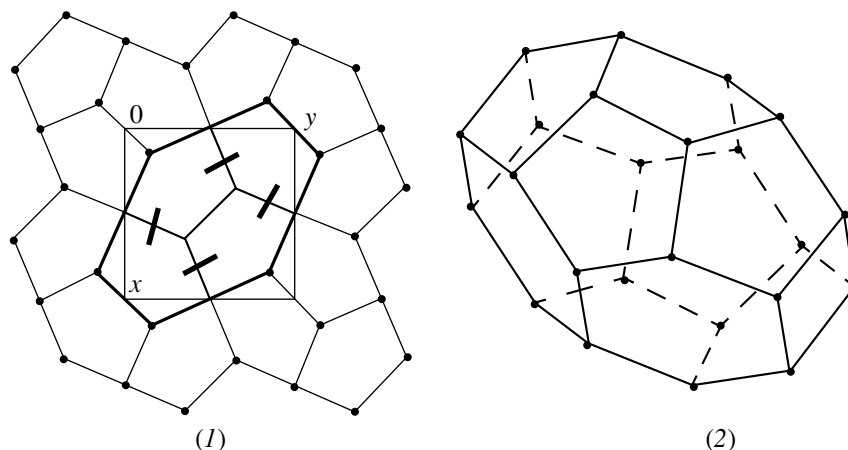
Fig. 2. (*1*) Packing of tetradecahedral cavities in the gas hydrate structure. The center of the cavity outlined with thick lines is located at the point with the coordinate $z = 0.5$; for the centers of the remaining cavities, $z = 0$. (*2*) A general view of the tetradecahedral cavity in the new structure.

pensates for this loss so that this structure is realized under pressure. In addition, each cavity contains only two tetragonal faces, whereas another space-filling polyhedron, a truncated octahedron (cavities of this shape are encountered in clathrate hydrates; however, the host lattice in this case is not a purely aqueous one), has six tetragonal faces per cavity. The O–O distances (hydrogen bond lengths) in this structure are within 2.64–3.04 Å, and the OOO angles are within 90.0°–129.9°. The distance between the argon atoms in a cavity is 3.25 Å. The shortest Ar–O distance is 3.50 Å. Taking into account the errors in our experimental data, we consider the scatter of parameters char-

acterizing the water lattice to be similar to that obtained for high-pressure ice modifications [13]. The distance between the argon atoms in a cavity is shorter than the sum of their van der Waals radii, which calls for special consideration.

Most likely, the same structure is also realized in the tetrahydrofuran–water system for the hydrate stable at pressures above 4.9 kbar. We obtained tentative data from the neutron powder diffraction pattern of this hydrate at about 11 kbar and room temperature. One of the variants of indexing this pattern corresponds to the tetragonal system with the unit cell parameters $a = 6.4$ Å

Coordinates of basis atoms in the structure of argon hydrate

Atom	x	y	z
O(1)	0	0.5	0.25
O(2)	0.147(3)	0.147(3)	0.643(3)
D(1)	0.109(4)	0.281(3)	0.659(2)
D(2)	−0.041(5)	0.615(3)	0.290(2)
D(3)	0.175(2)	0.175(2)	0.541(2)
D(4)	0.944(3)	0.944(3)	0.374(2)
Ar	0.181(5)	0.181(5)	0

and $c = 10.8$ Å. In addition, the hydration number (about five water molecules per guest molecule), determined from the maximum at the congruent melting curve in the T,x-section of the phase diagram for this hydrate [6], is similar to the value calculated implying ideal stoichiometry in the new structure (six water molecules per cavity). The molecular dimensions of the tetrahydrofuran molecule match the size and shape of the cavity.

Therefore, the above-described new structure is the fourth currently known polyhedral structure of gas hydrates that can be realized in many clathrate-forming guest–water systems at high pressures.

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