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Guest disorder and high pressure behavior of argon hydrates

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ABSTRACT

The structure of argon hydrate was studied at ambient pressure and low temperature, and between 1.7 and 4.2 GPa at 295 K. This analysis produced a single Ar guest atom, positionally disordered off-center in the large cages of sII. Above 1.7 GPa Ar clathrate transformed to a mixture of a body-centered orthorhombic filled-ice phase, which can be viewed as a polytype of ice-Ih, and high pressure forms of pure ice. The guest disorder is further substantiated by analysis of the guest to host ratio in this high pressure filled-ice structure. The bulk modulus of Ar filled-ice found to be 11.7 ± 0.4 GPa.

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1. Introduction

Extensive studies of clathrate hydrates have been conducted ever since the discovery of natural gas hydrates in pipelines [1]. Additionally, clathrate hydrates are found in permafrost and continental shelves and possibly even as a component of icy bodies in the outer solar system [2]. These compounds are formed by hydrogen-bonded water molecules that form cages, which stack to fill space and create a crystal lattice. These cages are stabilized by trapping guest species such as methane or noble gases. The later are good X-ray scatters and have more regular shapes than gas molecules, and as such, the clathrate hydrates formed by noble gases are significant model systems for the study of gas–water interactions essential for energy science.

Clathrate hydrates usually form three basic crystallographic structures, two are cubic and are known as structure I (sI) and structure II (sII) with space groups $Pm\bar{3}n$ and $Fd\bar{3}m$, respectively, and the third is hexagonal and known as structure H (sH) with $P6/mmm$ space group. As summarized in previous reviews [3,4], guest molecules tend to occupy different cages as their size increases. From the smallest to largest cage the sequence progresses from the dodecahedron (D, 5^{12}) and tetrakaidecahedron (T, $5^{12}6^2$) in sI, to the hexakaidecahedron (H, $5^{12}6^4$) in sII, to the largest icosahedron (E, $5^{12}6^8$) in sH. The notation $5^{12}6^2$ for example denotes a single polyhedral cage composed of 12 five-membered rings and 2 six-membered rings of water molecules, this cage type is common to all three hydrate structures. The general relationship of guest size to cage size enables a rough prediction of the expected clath-

rate structure for any given guest. However exceptions are known and perhaps the most notable are argon and krypton clathrates. Both argon (van der Waals diameter of 3.8 Å) and krypton (van der Waals diameter of 4.0 Å) atoms form sII hydrates yet these guests are smaller than, for example, methane (van der Waals diameter of 4.36 Å) and Xe (van der Waals diameter of 4.58 Å), which are both known to form sI. As shown in Fig. 1a, sII contains 16 dodecahedral cages and 8 hexakaidecahedral cages in the unit cell [5]. The larger free volume of guest within the cage allows the argon and krypton atom positions to be more disordered. Disorder of the guest species is important for understanding guest–host interactions in clathrate hydrates. For example, the location of the guest gives an indication of the potential surface within the cage, and as such, positional disorder of the guests may be related to the guest motions and anomalous thermal conductivity of clathrate hydrates. However, the details of any possible connection between guest disorder and thermal conductivity remain to be explored more completely. Furthermore, the simple atomic geometry of the inert gas guest atoms over other molecular guests reduces the complications associated with formulating models to fit the data [6]. A structural investigation of this disorder is the subject of this study.

The phase diagram of Ar–H₂O system established by Manakov et al. [7] indicates that Ar clathrate hydrate transforms from the sII form to the sH form at 0.46 GPa, then to a tetragonal phase at 0.77 GPa and finally transforms to a filled-ice structure above 1 GPa. Studies by Hirai et al. [8], conducted at about the same time did not report the observation of the hexagonal phase. The filled-ice structure in the argon system is analogous to that discovered in methane hydrate [9], in which the water molecules arrange to produce channels formed by an alternate stacking of six-membered ring layers slightly different to that in ice-Ih, and with the channels filled with Ar atoms, as shown in Fig. 1b.

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Fig. 1. The structures of (a) sII and (b) filled-ice for Ar hydrates. The cubic sII unit cell contains 16 dodecahedra ($D, 5^{12}$, blue) and 8 hexakaidecahedra ($H, 5^{12}6^4$, yellow) formed by water molecules surrounding Ar atoms at the center. The filled-ice structure is similar to the methane MH-III [9], Ar atoms are located in the channels of the water framework, note axes orientations are different from [9], the a -axis parallels the channel direction corresponding to the c -axis channel in the Ih structure. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Kuhs et al. studied Ar hydrate by neutron scattering and found it has sII form at 0.3 GPa and 260 K, and the large cages are singly occupied with guest disorder indicated by large thermal parameters [10]. The later work by Manakov et al. (also by neutron scattering) concluded that the large cage of the sII form contains, on average, two argon atoms [7]. Noticeably, the free volume of this cage (6.66 Å in diameter [3]) is smaller than the size of two adjacent argon atoms (2×3.8 Å, [11]), and thus this proposed double cage occupancy seems too high. Molecular dynamics calculations found double occupancy may be stabilized by external pressure, but with severe distortion [12]. A detailed description of the sII argon guest positional disorder and the structure of the higher pressure filled-ice remains to be adequately determined. Here we further describe the guest positional disorder in the sII hydrate using Rietveld refinement and MEM techniques [13] and extend this analysis to the higher pressure filled-ice structure between 1.7 and 4.2 GPa at 295 K.

2. Methods

Structure II Ar clathrate hydrate samples were produced at the National Research Council of Canada, Steacie Institute for Molecular Sciences using a method outlined previously [14]. The X-ray diffraction (XRD) of the as-synthesized sample was measured on a PANalytical Xpert diffractometer at the Center of Nanophase Materials Sciences, Oak Ridge National Laboratory, using Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å) with Bragg–Brentano geometry. The sample was first cold-loaded into the low temperature cryo-stage together with liquid nitrogen, excess liquid nitrogen was boiled off after sample loading and the chamber cover replaced. The XRD patterns of the sII structure were measured at ambient pressure from 100 K up to 138 K at scattering angles of $5^\circ < 2\theta < 120^\circ$.

For the complementary *in situ* high pressure experiments, the sample was also loaded in liquid nitrogen vapor at 77 K into a diamond anvil cell along with a small ruby chip for pressure determination, pressurized to 1.7 GPa to stabilize the sample, and then the temperature was raised to room temperature. Pressures were determined by the ruby fluorescence method [15]. X-ray diffraction data were measured using high energy synchrotron X-ray

(80.7 keV, $\lambda = 0.1537$ Å) at sector 1-ID of the Advanced Photon Source at Argonne National Laboratory. The diameter of the gasket hole was 250 μm and the beam size was 20 μm . Using a GE amorphous silicon area detector, data were recorded over a pressure range 1.7–4.2 GPa, one-dimensional images were obtained using the Fit2D software package [16].

A combined Rietveld and maximum entropy method (Rietveld/MEM) was applied to analyze the data. A series of programs, including RIETAN [13] for Rietveld refinement of the structure, PRIMA [17] for calculating electron density by MEM using results from RIETAN, and VESTA [18] for plotting the structure and density maps, were used. The Rietveld/MEM is a powerful tool for structure determination of complicated materials, e.g., the proton ordering in sI methane hydrate at low temperature has been studied using this method [19]. Data were first fitted in RIETAN, using a polynomial background with up to 12 terms, and pseudo-Voigt peak profile functions. RIETAN output around 129 observed reflections ($\sin \theta/\lambda \leq 0.47$) from the XRD data, and 255 observed reflections ($\sin \theta/\lambda \leq 0.7$) from the synchrotron X-ray data, which were used by PRIMA to calculate electron density map.

3. Results and discussion

The decomposition temperature of argon hydrate at ambient pressure is 147 K [20], thus over the measured temperature range (110–138 K) the samples were within the stable region of sII. Fig. 2 shows the pattern measured at 100 K along with the refined model [13]. The data were refined with two phases, sII with a lattice parameter of 17.11 Å [4] and ice-Ih [21]. The weight fraction of ice-Ih was $\sim 3.8\%$ at 100 K but increased to 9.0% at 138 K. The increasing ice fraction was most likely due to condensation and freezing of atmospheric water onto the sample and cryo-stage, because the sample chamber was not perfectly sealed during the data collection.

Initially, the sII phase was modeled with the Ar atoms located at the cage center, $16d$ ($5/8, 5/8, 5/8$) for the small cage and $8a$ ($0, 0, 0$) for the large cage. The overall refinement was considered good (with $R_{wp} = 4.8\%$), but the Ar atom at the $8a$ site had an anomalously large atomic displacement parameter of $B = 81$ Å²,

Fig. 2. XRD (Cu K α) of the sII Ar clathrate hydrate at 100 K. The + symbols denote the observed intensities; solid line, Rietveld refinement result; tick marks, peak positions for Ar clathrate hydrate (upper) and ice-Ih (lower); bottom curve, difference of ($I_o - I_c$).

and the site occupancy was refined to 1.23. Although the site occupancy seemed consistent with previous neutron scattering results where more than one atom was located in the large cage [7], the neutron scattering cross section of Ar is small, so the overall neutron datasets were only weakly weighted by the Ar guest. The refined O–O bond length is reasonable and between 2.72 and 2.77 Å, which also excludes doubly occupancy of the large cages as there is no severe distortion of the host framework [12]. This bond distance and interpretation of cage occupancy is also consistent with the work of Kuhs et al. [10]. An accurate model is required since the atomic displacement parameters and site occupancies are somewhat correlated in the refinements. Since Ar atoms are small, a certain degree of positional disorder is to be expected, particularly in the large sII cage at low temperature. This positional disorder may be manifested as a non-spherical shape of the electron density distribution of the guest atoms. Fig. 3a shows the electron density map around the Ar atoms, as generated by RIETAN/MEM, inside the large cage as viewed from the (1 $\bar{1}$ 1) direction. The complicated shape of this electron density map indicates the Ar atom positions inside the large cage are highly disordered.

Previous studies on the guest disorder in methane hydrates [19,22] indicated that the guest positions are constrained by the geometric shape of the cages. A tetrahedral site with vertices pointing to the center of the hexagonal faces [site 1, $32e(-x, x, -x)$] was subsequently used to model the guest locations, however, while the isotropic B was reduced somewhat, it was still found to be anomalously large (20 Å^2). Building on this idea, and after further observation of the MEM-derived guest electron density distribution, a model with the guest atoms distributed over two sets of tetrahedral sites, one as described above, and a second with each of its vertices pointing to a vertex of three edge sharing pentagonal faces of the cage [site 2, $32e(y, y, -y)$], was tested. This model is shown in Fig. 3b and the electron density calculated from partitioned intensities by MEM is shown in Fig. 3c. The refinement results for sites 1 and 2 give $x = 0.0518$ and $y = 0.0319$, and while the R_{wp} increased slightly to 5.3% the value of isotropic displacement parameter was much more reasonable ($B = 6.3 \text{ Å}^2$). The site occupancies for the small and large cages were 0.85 and 0.88, respectively, and within the large cage the site occupancies for sites 1 and 2 were 0.097 and 0.125, respectively, suggesting there

Fig. 3. (a) Electron density map of the guest atom in the large cage of Ar sII clathrate, from Rietveld/MEM using the model with one Ar atom at the center; (b) model with two sets of tetrahedral positions in the large cage, magenta—pointing to the center of hexagonal face, blue—pointing to the vertex of three pentagonal faces; (c) electron density map of guest atoms in the large cage, from Rietveld/MEM using the model with two split sites. White circles—Ar atoms, green isosurface—electron density at level of 0.5 electron/Å^3 , viewed along (1 $\bar{1}$ 1). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

was a slight preference for the pentagonal vertexes. The refined O–O bondlengths were 2.72–2.77 Å, and the nearest Ar–O distance is 3.46 Å for site 1 and 3.75 for site 2. The molar ratio of O to Ar atoms is about 6.5, which is similar to that of other noble gas hydrates [23,24] and significantly different from the value of 4.5 reported previously [7].

Since we increased the pressure on the sII hydrate directly to 1.7 GPa, the intermediate phase transformations were missed

and the clathrate framework decomposed to form a filled-ice structure. The filled-ice is a body-centered orthorhombic phase, where Ar atoms are located in the channels formed by water framework, as has been observed previously for methane hydrate [9]. Using high energy synchrotron X-ray diffraction at the APS, data over a large momentum transfer ($Q = 4\pi \sin \theta/\lambda$) range were collected and Bragg peaks up to $Q_{\max} = 12 \text{ \AA}^{-1}$ were identified. The data are fitted by the Rietveld method, as shown in Fig. 4a. The data collected at 1.7 GPa was fitted with two phases, Ar hydrate with the filled-ice structure [9], and the tetragonal ice VI [25]. At 1.9 GPa, the sample contains a mixture of ice VI and ice VII [26] and all data collected above 2.4 GPa can be refined with a mixture of the filled-ice structure and ice VII. The sample was a subset of the sample used for the high energy ambient pressure measurements in the cryostat, therefore the initial ice content is expected to be low, and since the sample was loaded into the diamond anvil cell held over boiling liquid nitrogen the excess ice we see in the sample chamber is likely the result of decreased water to guest ratio in the filled-ice form of the Ar hydrate.

Loveday et al. provided a detailed description of the filled-ice structure, comparing and contrasting it to the Ih ice structure [9]. Here we give a simpler view based on different layer-stackings of the hexagonal hydrogen-bonded sheet. The filled-ice structure (space group *Imma*) consists of puckered sheets of hydrogen-bonded six-membered rings of water molecules, which form the *bc* plane in Fig. 1b. This sheet is identical to that in ice-Ih, however, the layer stacking of these sheets is quite different in the filled-ice structure. In ice-Ih the hydrogen-bonded sheets alternately stack with $\pm 60^\circ$ rotation, whereas in the filled-ice structure the sheets alternately stack with 180° rotation. In this sense, the framework of the filled-ice structure can be simply viewed as a polytype of the ice-Ih structure. Nevertheless, the framework of the filled-ice structure is unique and has no analog in the known ice polymorphs. The layer stacking in the filled-ice structure creates a zig-zag chain of four-membered water rings between the layers, as can be seen in Fig. 1b. Channels are created in the *b* and *a* directions. The orthorhombic unit cell of the filled-ice structure

(subscript o) can be expressed in terms of the hexagonal unit cell of ice-Ih by the expressions, $\mathbf{a}_o = \mathbf{c}_h$, $\mathbf{b}_o = -\mathbf{a}_h + \mathbf{a}_h$, and $\mathbf{c}_o = \mathbf{a}_h + \mathbf{a}_h$. In the filled-ice model, the Ar atoms are located at site 4e (0, 1/4, -0.167) and O at site 8h (0.174, 1/4, 0.407), which gives an ideal stoichiometry of $\text{Ar}(\text{H}_2\text{O})_2$. The Ar atoms have their closest approach to each other in zig-zag chains running along the *b* direction. The refined *B* of the Ar atom decreased from $3.95 \text{ \AA}^2$ at 1.7 GPa to $2.75 \text{ \AA}^2$ at 4.2 GPa, indicating little or no disorder as compared to the Ar in the sII clathrate. The occupancy of Ar site was slightly deficient, varying slightly around 0.79. The resulting ratio of oxygen to argon atoms of the filled-ice was 2.57, which did not change significantly over the pressure range of the experiment. This is a much lower ratio than that found in the initial sII clathrate material. However, by including the mixed ice VI/VII from the multi-phase refinement, the total oxygen to argon ratio of the overall system increases to 6.2, which is close to that of the original sII low pressure composition. There was no evidence for any solid Ar in the system. This further substantiates the disordered site model for the sII form and leads us to the conclusion that the excess water was ejected from the sample upon phase transformation at high pressure and not deposited during the sample loading procedure.

Details of the refined parameters of the filled-ice structure are given in Table 1 and the lattice parameters are plotted in Fig. 4b. The *a*-axis was more compressible than both the *b*- and *c*-axes. At around 3.2 GPa, the unit cell became metrically tetragonal. This anisotropy in compressibility has also been reported in methane filled-ice [27]. The distance between Ar atoms ($\sim 3.5 \text{ \AA}$) was nearly constant over this pressure range and likely indicates hard sphere repulsion between the guest atoms. The van der Waals diameter of Ar was $3.76 \text{ \AA}$. The nearest neighbor Ar–Ar distance would correspond to that in solid argon at 20 GPa. By observation of the structure given in Fig. 1b it seems evident that the Ar–Ar repulsion stiffened both the *a*- and *b*-axes, while the *c*-axis, which is affected less by the Ar–Ar repulsion, is more compressible.

The pressure–volume data of the Ar filled-ice fitted with the Birch–Murnaghan equation of state ($P = 1.5B_0[(V_0/V)^{7/3}$

Fig. 4. (a) Measured X-ray scattering data (black) and that calculated (red) from Rietveld refinement of models for Ar clathrate hydrate under high pressure. Measuring sequence is from bottom to top. $\times$: original data; —: Rietveld refinement; $| \cdot |$: peak positions for Ar filled-ice phase, ice VI and ice VII, respectively. The peak from 4.2 to 4.45 is from the gasket and has been excluded from the refinement. (b) Variations of the lattice parameters. The open symbols are for decompression. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Refined structural parameters for Ar hydrate as a function of pressure.

P (GPa)	Filled-ice							Ice VI			Ice VII		Rwp (%)
	a (Å)	b (Å)	c (Å)	O:Ar	O–O (Å)	Ar–O (Å)	Ar–Ar (Å)	a (Å)	c (Å)	wt.%	a (Å)	wt.%	
1.7	7.973(2)	4.696(1)	7.771(2)	2.51	2.74*	2.79	3.29	3.60	3.51	6.108(2)	5.609(2)	42.5	3.5
1.9	7.959(2)	4.700(1)	7.785(3)	2.51	2.70	2.78	3.29	3.60	3.53	6.110(3)	5.613(3)	28.6	4.2
2.4	7.835(5)	4.658(3)	7.731(5)	2.57	2.71	2.74	3.25	3.56	3.48		3.338(2)	41.1	4.2
2.9	7.750(3)	4.631(1)	7.709(3)	2.56	2.70	2.71	3.23	3.53	3.48		3.321(1)	36.7	4.0
3.8	7.607(4)	4.582(2)	7.668(3)	2.50	2.67	2.71	3.16	3.48	3.49		3.290(1)	35.1	4.3
4.2	7.549(4)	4.571(2)	7.659(3)	2.60	2.65	2.71	3.14	3.46	3.49		3.279(1)	35.2	4.1
3.1(1)	7.717(2)	4.628(1)	7.709(2)	2.67	2.67	2.73	3.22	3.52	3.48		3.317(5)	39.5	3.7

* Note: errors for all bond-lengths are within 0.01 Å.

Fig. 5. Birch Murnaghan fit of P – V data for (a) Ar filled-ice and (b) ice VII.

$-(V_0/V)^{5/3}[1 + 0.75(B'_0 - 4)((V_0/V)^{2/3} - 1)]$ [28] are plotted in Fig. 5a. The point for 1.9 GPa was excluded from the fitting because of its lower accuracy as the pattern was refined with three phases at this pressure. For this pressure range we assume a linear P – V relationship and B'_0 is fixed at 4. The fitting results shows that the unit cell volume for Ar filled-ice at zero pressure (V_0) should be around 317 Å³, and the bulk modulus at zero pressure (B_0) is 11.7 ± 0.4 GPa, which is greater than that of ice-Ih (8.97 GPa [29]). Previously, the bulk modulus of methane filled-ice was calculated by Hirai et al. [27] (15.4 GPa) and Loveday et al. [30] (15.2 GPa). These values indicated the stiffening effect of Ar is less than for methane, which might be expected given the smaller size of Ar compared to methane.

We used the presence of ice VII as an internal standardization of our results, given its known equation of state. The B_0 for ice VII was found to be 14.3 ± 0.8 GPa with B'_0 fixed at 4.0, as shown in Fig. 5b. The fitted zero-pressure unit cell volume (V_0) is 41.1 Å³, corresponding to 3.45 Å for the lattice parameter, which agrees with previous results [31]. Our result for B_0 is in general agreement with the 14.9 GPa reported by Shimizu et al. [32], and is close to Munro's result of 15.8 GPa [33]. Others have reported the B_0 of ice VII was reported to be above 20 GPa [31,34] for measurements taken over a much larger pressure range.

4. Conclusions

We studied both low and high pressure forms of argon clathrate hydrate by X-ray diffraction. Based on the electron density map obtained using Rietveld methods and MEM, a two-site tetrahedrally split model was used to simulate the disorder of the guest atoms

inside the large cage of sII. This disordered model results in site occupancies of 0.85 and 0.88 for the small and large cages, respectively, therefore the cages are singly occupied, which is in agreement with atomic size and cage volume constraints. This result contrasts to previous reports of an average large cage site occupancy of two. The high pressure form of argon hydrate was studied by synchrotron X-ray diffraction. The diffraction data collected above 1.7 GPa could be well modeled with a mixture of a filled-ice structure containing Ar atoms and either ice VI or VII. Overall the oxygen to argon ratio after the transformation to filled-ice supports the assignment of one atom per large cage in the sII Ar clathrate. The Ar filled-ice structure is the same as the methane filled-ice structure reported by Loveday et al. [30] and thus constitutes another example of this unique hydrogen-bond topology only known from high pressure. Both the methane and argon filled-ice forms become stable above 1.9 and 1.7 GPa, and cannot be quenched to ambient pressure. The framework of the filled-ice structure can be viewed as polytype of the hexagonal ice structure. Repulsion between neighboring Ar atoms and the presence of four-membered hydrogen-bonded water rings effectively stiffened the filled-ice structure, resulting in a larger B_0 of 11.7 GPa compared with 8.97 GPa for ice-Ih, but is smaller than 15.2 GPa for methane filled-ice.

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