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The Crystallographic Structure of the Natural Air-Hydrate in Greenland Dye-3 Deep Ice Core*

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Abstract. We have carried out X-ray diffraction studies on single crystals of natural air-hydrate in deep ice cores recovered at Dye-3 Greenland. Integrated intensities for 470 diffracting planes were measured by an automated four-circle diffractometer. The space group determined is cubic *Fd*3*m* and the lattice constant is 17.21(3) Å. These results indicate that the crystallographic structure is the Stackelberg's structure II, in contrast to the previously anticipated structure. This finding agrees with the recent results on the synthetic air-hydrate by Davidson *et al.* It was also found by difference Fourier synthesis for guest molecules that electron density in a 16-hedral cage has multiple maxima displaced from the center of the cage while that in the 12-hedron was approximately spherical.

Key words. Air-hydrate, clathrate, ice core, guest molecule.

1. Introduction

The existence of an air-hydrate in ice was suggested by Miller in 1969 [1] and crystals of various shapes were first found by Shoji and Langway in ice cores from depths greater than 1280 m at Dye-3, Greenland, in 1982 [2]. Although we have determined the enclathrated gas to be O_2 and N_2 by observing the Raman spectra of the hydrates [3], the crystallographic structure has not been determined because of difficulties in measuring the X-ray diffraction intensities from the hydrate crystal. In the present study, however, we have made the first measurements of the X-ray integrated intensities from single crystals of air-hydrates by the use of an automated four-circle diffractometer (Rigaku AFC-6A).

Gas hydrates form water clathrates of two distinct crystallographic structures, Stackelberg's structures I and II. Structure I was suggested for the air-hydrate by Miller [4] according to the general rule that guest molecules with maximum van der Waals diameters up to 5.8 Å give structure I. Recently, however, Davidson *et al.* [5, 6] found that structure II is preferred for very small guest

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* Dedicated to Dr D. W. Davidson in honor of his great contributions to the sciences of inclusion phenomena.

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molecules such as Ar, Kr, O_2, and N_2. This finding suggests that very small guest molecules are preferentially enclathrated in the smaller cages (12-hedra) of structure II [5]. In addition, it was also suggested for such hydrates that the guest molecules in 16-hedral cages are not situated at the center of the cage [7]. In order to determine experimentally the site occupancies and electron densities for either cage, one must have recourse to single crystal X-ray diffractometry. Since most of the air-hydrates included in the Dye-3 deep ice core were found to be single crystals, the first attempt at clarifying both the site occupancies and the electron density distributions in air-hydrates is reported in the present study.

2. Experimental Procedure

The ice-cores at a depth of about 1500 m (core Nos. 1449 and 1550) were used for the present study because they contained many air-hydrate crystals with polyhedral shapes. Specimens of a dimension of $1 \times 1 \times 1\ \mathrm{mm}^3$ were carefully prepared by a microtome in a cold room at −20°C in such a way that only one air-hydrate crystal was included in each specimen. The ice surrounding the air-hydrate crystal had to maintain a sufficiently high pressure on the specimen so as to stabilize the air-hydrate. For this reason, the temperature of the specimen was always kept below −20°C to avoid plastic deformation of the surrounding ice. A typical example of the included air-hydrate crystal is shown in Figure 1. The specimen formed was placed on a fine glass tube attached to a goniometer head, being sealed by Mylar film and silicone oil to avoid sublimation, as shown in Figure 2. Since the air-hydrate crystal cannot be observed after sealing, precise setting of the crystal at the center of the goniometer was very difficult. After diffraction from

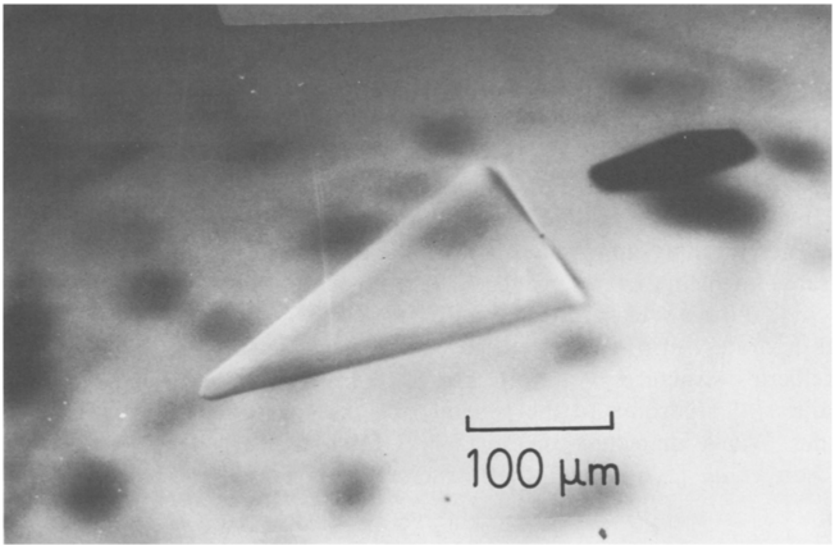

Fig. 1. A single crystal of air-hydrate embedded in a deep ice core.

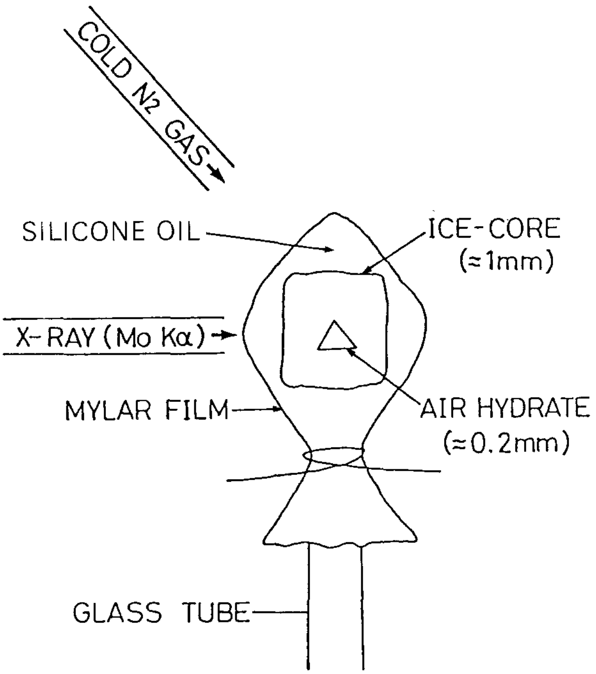

Fig. 2. A specimen mounted for AFC measurements.

the air-hydrate was found, centering was achieved by measuring the diffracted intensities.

Since the diffractometer was installed at room temperature, at about +20°C, a specially designed apparatus using a cold N_2-gas flow, was used for cooling the specimen without disturbing the measurements. The temperature of the specimen was kept at roughly −30°C during the measurements. The X-ray intensity measurements were made by MoK_α radiation generated from the X-ray diffraction tube (Toshiba 50 kV, 30 mA). A graphite monochromator was used.

First, diffraction peaks were automatically searched for 2θ angles between 11.8° and 15.2°, a region in which no peaks were expected from ice crystals but only from air-hydrate. On the basis of reciprocal lattice vectors determined from the peaks found, a tentative unit cell was formed. Adding other new peaks found in an angle range beyond 15.2° for given indices h, k, and l, allowed refinement of the unit cell. Secondly, the integrated intensities were automatically measured for the given indices for which 2θ was smaller than 40° on the basis of the refined unit cell. Although the maximum 2θ angle, limited by the diffractometer equipped with the cooling apparatus was 70°, no peaks with sufficient intensities were observed at 2θ angles larger than 40° with the specimen used. Structure factor data larger than three times their standard deviations were obtained for 470 diffracting planes. Since the hydrate crystal was surrounded by ice, an absorption correction to the structure factors was made for the ice of an assumed spherical shape.

3. Experimental Results

3.1. CRYSTAL DATA

The crystals are cubic with a lattice constant a = 17.21(3) Å at about −30°C, averaged over four different crystals. The hydrostatic pressure maintained by the surrounding ice was not known. During storage of the ice core the pressure is gradually released from its initial value of about 13 MPa. The space group is uniquely determined as *Fd*3*m* from the systematic absences of $(h\,k\,l)$ for $(h\,k\,l)$, $h+k,\ k+l,\ (1+h)=2n$; $(h\,h\,l),\ (l+h=2n)\circlearrowright$; $(0\,k\,l),\ (k,l=2n)$; $k+l=4n\circlearrowright$. Table I shows the relevant data upon which the structure II hydrate is based.

3.2. STRUCTURE REFINEMENT

Structure refinement was performed separately on two different specimens. Since no significant difference was found between the two, the result obtained for one specimen is described here. Structure factors for 470 reflecting planes were averaged over the equivalent diffracting planes and the data for 139 independent planes were obtained. However, some data were widely scattered even for equivalent planes. This scattering can be attributed to a planar shape of the hydrate crystal rather than a spherical one, absorption and reflections by the surrounding ice, and some misalignment of the crystal from the center of the diffractometer. For the structure refinement, therefore, data with low reliability were eliminated. Only the independent reflections with identical data for two or more equivalent planes were used. Finally, using the structure factors obtained for 52 independent diffracting planes, the least-squares refinement of the structure was made by a computer program MOLLY5 in the CHARGE system [8] starting from the positions of the water molecules determined by Stackelberg and Müller [9].

For guest molecules, a free rotor model [10] with the effective scattering factor $f = 2f_g \sin\phi/\phi$ with $\phi = 4\pi\rho \sin\theta/\lambda$ was assumed; where, for diatomic molecules, f_g is the atomic scattering factor and 2ρ is the distance between two atoms. This model corresponds to an N_2 (or O_2) gas molecule rotating freely around its center of mass. The averaged values of f calculated for N_2 and O_2 were used for the refinement. In order to determine the site occupancies of the guest molecules for either cage, *R* factors were minimized by varying the temperature parameters (five variable parameters) of both the oxygen atoms in the host lattice and the guest molecules for given values of the site occupancies.

Table I. Unit cells of clathrate hydrates [9]

	Structure I	Structure II
Cell size, symmetry	12.0 Å, *Pm*3*n*	17.2 Å, *Fd*3*m*
No. of larger cages, diameter	6, 5.9 Å	8, 6.9 Å
No. of smaller cages, diameter	2, 5.2 Å	16, 4.8 Å
No. of water molecules	46	136

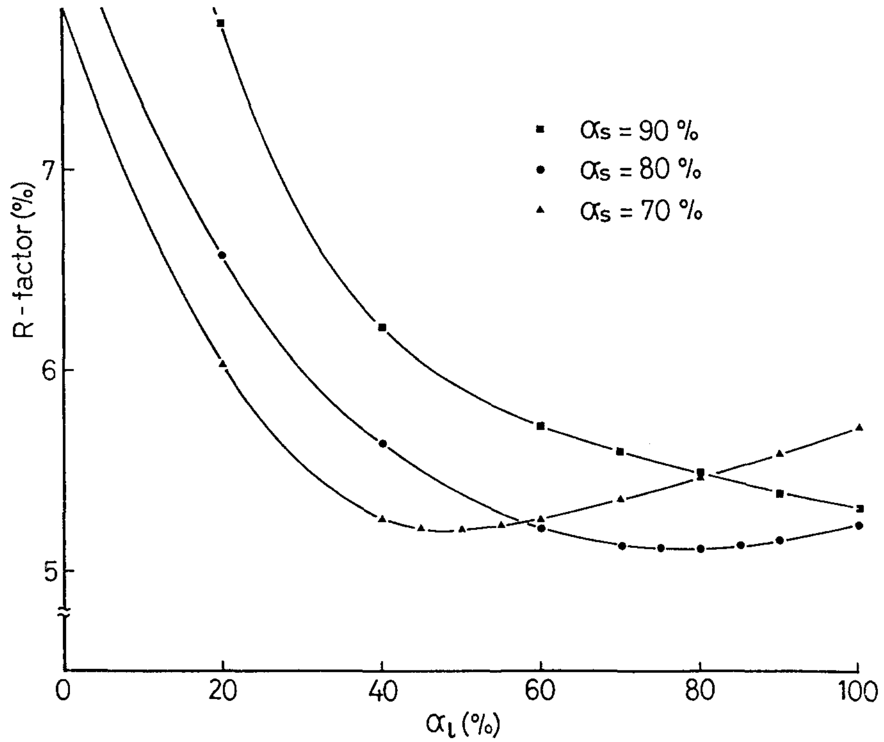

Fig. 3. *R*-factor as a function of site occupancies α_s for the smaller cages and α_l for the larger ones.

Figure 3 shows the minimized *R* factors as functions of the site occupancies α_s and α_l, where α_s is the site occupancy of the guest molecules for the smaller cages (12-hedra) and α_l is that for the larger ones (16-hedra). In the figure, the minimum value of *R* is 0.051 at $\alpha_s \approx \alpha_l \approx 0.8$. However, a small difference in *R* factors has no significant meaning due to the small number of independent reflections used. Therefore, considerable uncertainty must be included in the values of both α_s and α_l.

The positions of water molecules in a host lattice were also optimized for fixed values of α_s and α_l. Since the contribution of hydrogen atoms was very small, all parameters for hydrogens were fixed for the refinement as listed in Table II. For this refinement, therefore, nine variable parameters were used, including a scale factor. The most plausible atomic parameters are tabulated in Table II and observed and calculated structure factors are listed in Table III.

4. Discussion

To examine the free rotor model assumed for the guest molecule, difference synthesis was computed, which subtracted out the contribution of water molecules in a host lattice. Figure 4(a) and (b) show the central part of the electron-density distribution in 12- and 16-hedra, respectively. In 12-hedra, an approximately

Table II. Final atomic parameters

Atom	Site	x	y	z	Occupancy	B (Å^2)
Water						
O	8a	−0.125	−0.125	−0.125	1.0	3.0(8)
O	32e	−0.2165(5)	−0.2165(5)	−0.2165(5)	1.0	3.2(4)
O	96g	−0.1834(3)	−0.1834(3)	−0.3697(6)	1.0	3.7(2)
H	32e	−0.185	−0.185	−0.185	0.5	4.0
H	32e	−0.158	−0.158	−0.158	0.5	4.0
H	96g	−0.205	−0.205	−0.271	0.5	4.0
H	96g	−0.195	−0.195	−0.316	0.5	4.0
H	96g	−0.149	−0.149	−0.370	0.5	4.0
H	192i	−0.149	−0.034	0.153	0.5	4.0
Guest						
12-hedra	16c	0.0	0.0	0.0	0.80	5.0(1.1)
16-hedra	8b	0.375	0.375	0.375	0.75	33.3(5.8)

Table III. Observed and calculated structure factors

h	k	l	F_{obs}	F_{calc}	h	k	l	F_{obs}	F_{calc}
0	4	0	27.3	27.8	10	2	2	15.3	15.9
3	3	1	11.7	11.7	6	6	6	15.6	15.9
4	2	2	35.8	36.7	9	5	3	16.1	15.6
5	1	1	63.9	64.0	10	4	2	14.6	13.1
3	3	3	64.7	62.0	11	3	1	13.3	11.7
4	4	0	76.3	77.0	9	7	1	12.4	10.3
5	3	1	55.7	57.2	8	8	2	17.1	18.0
4	4	2	19.4	18.9	10	6	0	24.4	24.8
6	2	0	28.0	28.9	9	7	3	15.9	16.5
5	3	3	17.9	17.3	12	0	0	20.9	24.6
6	2	2	13.6	15.7	8	8	4	14.3	15.9
5	5	1	11.7	12.3	11	5	1	22.6	23.0
7	3	1	12.5	11.3	7	7	7	26.3	21.8
5	5	3	16.4	14.4	12	2	2	24.8	22.4
8	0	0	15.3	16.7	10	6	4	24.9	25.1
7	3	3	47.8	47.1	11	5	3	14.4	11.8
6	6	0	89.0	82.7	9	7	5	14.8	16.3
8	2	2	66.4	70.4	13	3	3	27.9	29.0
7	5	1	15.6	16.1	8	8	8	39.1	39.7
5	5	5	73.1	76.6	11	7	5	11.6	10.2
8	4	0	25.3	24.9	10	10	0	42.7	43.1
9	1	1	23.4	22.6	14	2	2	13.8	12.5
7	5	3	26.7	25.3	16	0	0	16.7	16.3
8	4	2	22.7	23.1	14	8	2	12.4	14.3
9	5	1	8.6	8.0	16	4	0	16.7	17.6
7	7	3	11.7	9.2	12	8	8	16.5	15.0

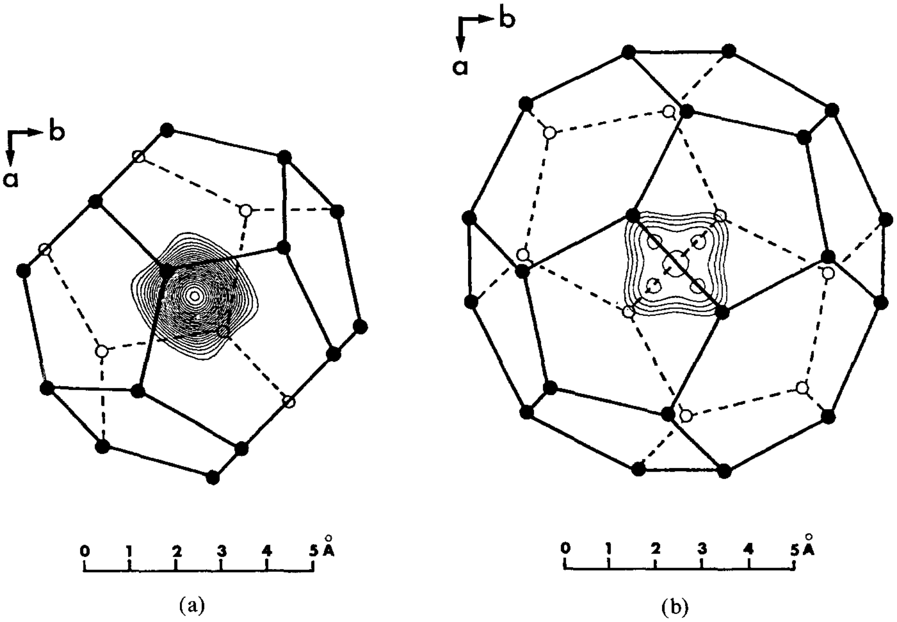

Fig. 4. Electron density section through center of the cages: (a) 12-hedron; (b) 16-hedron. Contours at 0.02-$e/\text{Å}^3$ intervals.

spherical distribution is located at the center of the cage. This distribution supports the model assumed. However, in 16-hedra, the distribution is significantly deformed from a spherical one and the electron density has multiple maxima in a cage. This implies that the center of the guest molecule in 16-hedra does not coincide with the center of the cage but is located around the center. Such a distribution of the guest molecule in 16-hedra was first proposed by Tse *et al.* from a very large temperature parameter for the guest molecule observed in the oxygen hydrate [7].

It is interesting to compare the present results with Raman scattering experiments of the air-hydrates included in the same ice core [3]. Since only a single peak was observed for each N_2 or O_2 stretching mode, the guest N_2 (or O_2) molecules should therefore be enclathrated in either 12- or 16-hedra. However, if the magnitude of the interaction between the guest molecules in 16-hedra and the surrounding water molecules is not significantly different from that in 12-hedra, a single peak can be observed even when both cages are occupied by N_2 (or O_2). Approximately equal site occupancies for both cages seem to support this expectation. Moreover, since the guest molecules in 16-hedra are displaced from the center of the cages, distances between the guest and the nearest water molecules in 16-hedra must be roughly equal to those in 12-hedra. It can therefore be expected that the stretching frequency of the guest molecule in 16-hedra does not differ from that in 12-hedra.

Tse *et al.* deduced the site occupancies α_s and α_l to be 0.8 and 1.0, respectively, on the basis of their neutron diffraction experiments on polycrystalline oxygen hydrates [7]. The values obtained in the present study coincide with those reported in [7], within the limits imposed by the errors involved. As discussed by Tse *et al.* [7], the large occupancy for the smaller cages explains the reason why structure II is favored.

Using the deduced site occupancies, the density and the hydration number, a number ratio of water molecules vs. guest molecules necessary to form a hydrate was calculated as 0.98 kg/m^3 and 7.1, respectively. Although the density has not been measured yet because the crystal cannot be separated from the ice crystal under atmospheric pressure, it is estimated to be slightly larger than that of ice on the basis of the difference in refractive indices between air-hydrate and ice [2]. Since the density of ice at $-30°C$ is 0.92 kg/m^3, the values calculated above are consistent with this estimation.

From the Raman intensities of the stretching modes of N_2 and O_2, the composition ratio of N_2 vs. O_2 included in one air-hydrate crystal was deduced to be 1.6 – 1.9 [3]. This enrichment of O_2 in the hydrate must be due to the lower dissociation pressure of O_2-hydrate than that of N_2-hydrate; i.e. O_2-hydrates should be formed at a shallower part of the ice-sheet where N_2-hydrates cannot be formed. However, no hydrate crystals have been observed at a depth where the pressure exceeded the dissociation pressure of O_2-hydrates but not that of N_2-hydrates, in the Dye-3 deep ice core [11]. Although this discrepancy can be attributed to difficulties in nucleation of the hydrate crystals in ice [11], the formation process of the air-hydrates in the ice sheet remains unsolved. For a better understanding of the process it is important to know both site occupancies and the composition ratios as a function of pressure.

In order to clarify the formation process and to allow further detailed discussion of the structure, more precise data are required, gathered over many independent reflections. However, improvement of the measurements is very difficult for natural air-hydrate. An attempt to grow a single crystal of N_2-, O_2- and air-hydrates under hydrostatic pressure is underway.

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