

Transition from Cage Clathrate to Filled Ice: The Structure of Methane Hydrate III

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(Received 22 March 2001; published 31 October 2001)

The structure of a new methane hydrate has been solved at 3 GPa from neutron and x-ray powder diffraction data. It is a dihydrate in which a 3D H-bonded network of water molecules forms channels surrounding the methane molecules. The network is closely related to that of ice-*I_h* and the methane-water system appears to be the first in which a cage clathrate hydrate is transformed into an ice-related hydrate (a “filled ice”).

DOI: 10.1103/PhysRevLett.87.215501

PACS numbers: 62.50.+p, 61.12.Ld

The existence of inclusion compounds involving water and hydrophobic species such as common gases and hydrocarbon molecules has long been recognized [1]. The majority of these compounds—known as clathrate hydrates—adopt one of three structures where the included guest species occupies cages formed by H-bonded networks of host water molecules [2]. These structures are believed to be stabilized by repulsive interactions between the guest and host molecules and the H-bonded host networks have no obvious relationship with known ice structures [3]. The guest-host interactions make clathrate hydrates model systems for the study of hydrophobic interactions relevant to problems in biology [4] and fundamental understanding of the water potential [5]. In addition, clathrate hydrates of gases such as methane, oxygen, carbon dioxide, and nitrogen are widely found in nature. Their behavior and properties are crucial to the understanding of processes both on Earth and in the outer solar system [6,7]. Most clathrate hydrates require at most modest pressures (of the order of a few hundred bar) to be stable. Work at higher pressures has revealed new gas hydrates in the helium- and hydrogen-water systems [8,9]. Helium hydrate and the two hydrates of hydrogen have been termed clathrates [8,9], but do not adopt any of the cage structures which are either observed or predicted for clathrate hydrates [2]. Instead they have structures related to ice-II [(H₂O)₆ · H₂ and (H₂O)₆ · He] [8,9] and ice-I_c (H₂O · H₂) [8], and thus differ markedly from the three widely adopted clathrate structures—in which the guest molecules occupy distinct cages whose diameters are much larger than the channels which connect the cages together. We will refer to these latter structures as “cage clathrates.” In the helium and hydrogen hydrates the guest molecules occupy channels—whose diameters do not vary markedly along their length—within a water network which is related to a known ice structure. These new clathrate hydrates might therefore be more accurately termed “filled ices.”

To date there is no obvious link between the cage clathrates and filled ices: hydrogen and helium are not

known to form cage clathrates and—although Raman and differential thermal analysis studies in the pressure range 0–3 GPa have revealed evidence of high-pressure transformations in argon, methane, neon, and nitrogen hydrates [10–14]—there has been no direct demonstration of new hydrate structures in any cage-clathrate-forming system [13]. Now, in methane hydrate (MH), we have found structural transformations from the low-pressure cage type-I clathrate form, MH-I [15], to two new hydrate phases, MH-II at ~1 GPa and then MH-III at ~2 GPa [16]. We show that the structure of MH-III can be viewed as a filled ice, and thus the methane-water system links the two classes of clathrate hydrates for the first time.

Samples of both hydrogenous (for x-ray studies) and fully deuterated [17] (for neutron diffraction studies) methane hydrate were produced by adsorbing methane into ice at 250 K as described by Handa [18]. Samples were loaded into a Merrill-Bassett diamond-anvil cell for the x-ray studies and a Paris-Edinburgh pressure cell [19,20] for the neutron studies at ~100 K. The cells were then sealed and warmed to room temperature. The pressure was increased from the initial sealing value of ~0.5 GPa to ~1.9 GPa. The deuterated samples transformed readily to MH-III when increased above this pressure, while in hydrogenous samples MH-III formed slowly over the course of ~12 h [16] at ~1.9 GPa. Neutron diffraction studies were carried out on the PEARL beam line of the U.K. neutron facility, ISIS, at the Rutherford Appleton Laboratory, and x-ray studies were carried out using image-plate techniques [21] on station 9.1 at the U.K. synchrotron source, SRS, at Daresbury Laboratory.

Figure 1 shows the diffraction patterns collected from samples of MH-III. Density considerations imply that MH-III has a 2:1 water-methane ratio [16]. Because the initial MH-I has a 5.75:1 water-methane ratio, these patterns are dominated by scattering from the ice VII that is formed by the 3.75 free water molecules released for every two in the MH-III. However, numerous peaks from MH-III can be identified. With the exception of the two

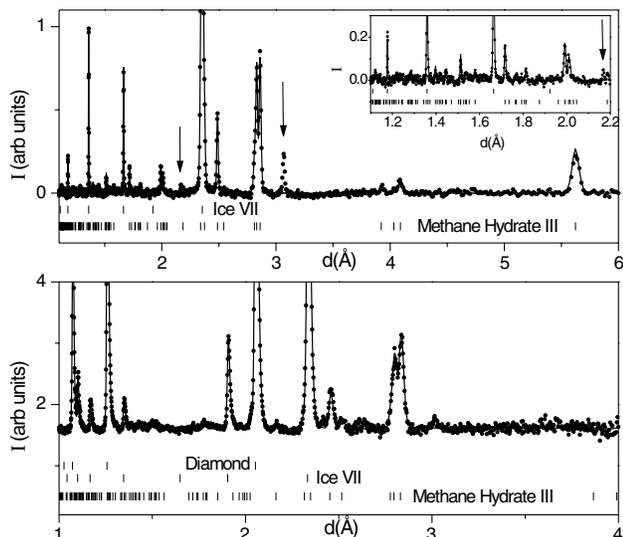


FIG. 1. Data collected from ice-VII and MH-III at 3.0 GPa and room temperature with x-rays (upper plots) and neutrons (lower plot). The inset reproduces the short d -spacing part of the x-ray pattern with an expanded scale. The observed data are shown as dots and the calculated profile as a solid line. The tick marks denote the calculated positions of the diffraction peaks from MH-III, ice-VII, and—in the case of the neutron data—scattering from the sintered-diamond anvils. The arrows in the upper plot and inset mark two additional peaks discussed in the text.

arrowed peaks in the x-ray pattern, all peaks observed can be indexed as MH-III, ice-VII, or sintered diamond from the pressure cell (in the neutron case). (The arrowed peaks do not move with pressure at the same rate as those from ice-VII or MH-III and cannot be indexed as methane [22]. They are attributed to a further minority methane hydrate phase.) The systematic reflection absences are consistent with space groups $Imcm$ and $I2bm$. Density considerations require four methane molecules in the unit cell and so $I2bm$ was chosen as the initial space group because it has the lowest symmetry fourfold site. Initially, the methane molecules were placed as far apart as possible on $1/4, 0, 0$ sites. The oxygen atoms were then found from Fourier difference maps. Further refinements could be made stable only by fixing the oxygen atoms at $x = 1/4$. This implies that the symmetry of the heavy-atom structure is $Imcm$.

Each oxygen atom has four neighboring oxygen atoms at a plausible distance to be hydrogen bonds, ~ 2.8 Å, and space group $Imcm$ implies that these hydrogen bonds be disordered—four half-occupied H(D) sites around each oxygen atom. However, a stable fit to the neutron data could not be obtained using a proton-disordered structure and so a number of possible proton-ordered structures were explored. Only one maintains the b - c mirror planes of the heavy-atom structure. This arrangement, in space group $Pm\bar{c}n$, has two nonequivalent water molecules. The atoms of one type of molecule all lie in the b - c mirror plane so that, for example, oxygen atom 1 in Fig. 2(a) donates H bonds to atoms $1'$ and 6. The second type of molecule has

its H atoms related by reflection in the b - c mirror plane, such as oxygen atom 2 which donates H bonds to atoms 1 and 3. Fits using this structure were stable for both the neutron and x-ray data, and showed a marginal improvement of the fit to the neutron data but no improvement of the fit to the x-ray data. Thus the evidence for a proton-ordered structure is marginal but it cannot at present be ruled out. Full resolution of the question of proton ordering is likely to require neutron data from a sample composed solely of MH-III, if a way can be found to make such a sample. (As explained, MH-III samples made by compressing MH-I unavoidably contain a large amount of free ice.) However, the state of proton ordering does not significantly alter the structure and the conclusions to be drawn. The final refinements [23] shown in Fig. 1 and the distances in Table I were obtained using a proton-disordered structure in space group $Imcm$. Also included were four H(D) atoms placed on the C site with a large thermal motion to approximate the scattering from the presumed rotationally disordered methane molecules. As can be seen, the quality of the fits is good and the interatomic distances (Table I) are plausible.

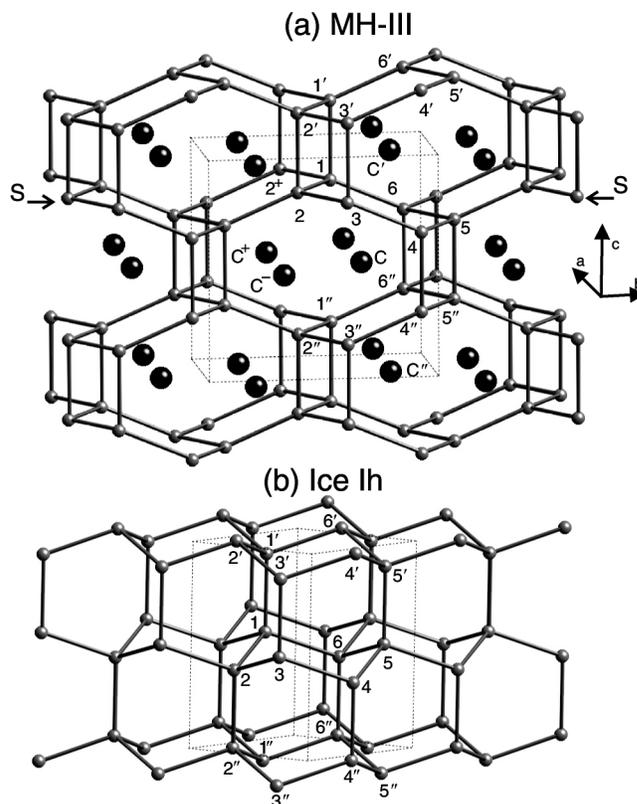


FIG. 2. The structure of (a) MH-III and (b) ice-Ih viewed perpendicular to their c axes. The smaller spheres are O atoms of the water network and the lines denote H bonds. The larger spheres in (a) are the methane molecules. MH-III is viewed approximately along its a axis and ice-Ih is viewed approximately along a $[110]$ direction. A given symbol with single, double, or no prime denotes atoms related by translation along the c axis; superscripts + and - in (a) mark related atoms displaced along $\pm a$.

TABLE I. Selected bond lengths in MH-III at 3.0 GPa.

From	To	Length Å
C	C', C''	4.053(6)
C	C ⁺ , C ⁻	3.852(21)
O1	O1'	2.811(10)
O1	O6	2.807(14)
O1	O2, O2 ⁺	2.783(9)
C	O4, O6, O4'', O6''	3.297(10)
C	O2, O2''	3.359(13)
C	O5, O5''	3.544(4)
C	O1, O3, O1'', O3''	3.552(4)

The heavy-atom structure of MH-III is remarkably similar to that of ice-*Ih* when viewed along the *c* axes (Fig. 3). The H-bonded water network is composed of puckered *a-b* sheets of edge-sharing six-membered rings of water molecules—such as *S* in Fig. 2—which are cross linked along *c*. The rings form hexagonal channels running along the *c* axis, and the methane molecules sit between the *a-b* sheets close to the axis of these channels. At first glance the structures look significantly different when viewed perpendicular to *c* (Fig. 2). However, closer inspection of the rings (for example, those labeled 1, 2, 3, 4, 5, and 6 in both structures) reveals that the difference is relatively small and principally concerns the H bonds formed along the *c* axis by oxygen atoms 2 and 5. In ice-*Ih* they H bond to oxygens 2'' and 5'. In MH-III, they bond in the opposite directions along *c* to oxygens 2' and 5'', while the general topology of all the other H bonds remains the same in the two structures. The reversal of these H-bond directions (see (+) and

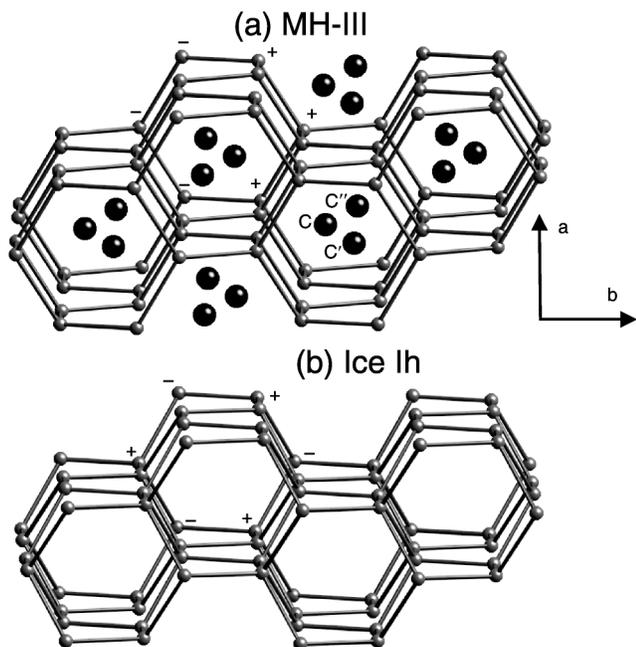


FIG. 3. The structure of (a) MH-III and (b) ice-*Ih* viewed parallel to their *c* axes. The (+) and (-) symbols show the sense of *c*-axis H bonds from the puckered sheet labeled *S* in Fig. 2.

(-) in Fig. 3) means that in MH-III the frequency along the *a* axis of interlinking *c* axis H bonds is roughly doubled relative to the frequency in the corresponding direction in ice-*Ih* and the frequency along the *b* axis is halved. As a result, instead of the three intersecting channels at 60° intervals perpendicular to *c* found in ice-*Ih*, MH-III has only one channel perpendicular to *c* which is directed along the *a* axis. The channels are much larger than those of ice-*Ih* because of the halving of the interlink frequency along *b*—there is no bond between oxygens 5 and 5', for example; these channels are equivalent to two adjacent ice-*Ih* channels. We can thus regard the H-bond network of MH-III as a distortion of the ice-*Ih* network, where one set of channels perpendicular to *c* is expanded to accommodate the methane molecules within the structure.

The need for this expansion is made clear by an examination of the interatomic distances. Each methane is twelvefold coordinated and the shortest C...O distances in MH-III are the six at ~3.3 Å in Table I. By comparison, if methane could occupy sites in the channels of ice-*Ih* then the corresponding distances would be only ~2.9 Å even at ambient pressure [24]. To relieve this implausibly short distance within the ice-*Ih* topology would require an implausibly large (>10%) increase in some H bond lengths. In MH-III, the doubling in size of the *a*-axis channels (see above) and the increase of ~0.4 Å in the maximum width of the channels along *c* (from 5 to 5') allow closer packing of the methane molecules by displacement along *b* towards the center of the *a* axis channels. They are then offset from the centers of the channels running along *c*, giving the zigzag arrangement of methane positions—for example, from C' to C to C''—visible in Fig. 3(a). This displacement lengthens the shortest C...O contacts and reduces the shortest C...C distance. Given that the latter (from C to C') is close to the value found in methane I at the same pressure [22], it appears likely that the balance between O...C and C...C repulsions determines the location of the methanes. It should be noted here that the O...C distances are much shorter than in the low-pressure structure-I methane hydrate (by ~0.5 Å). Furthermore, if there is a C-H bond directed along the short C...O contacts then the H...O distances would fall well within the upper limit for weak C-H...O hydrogen bonds [25].

The distortion of the ice-*Ih* water network to achieve reasonable C...O distances involves very little change in the H-bond lengths (only 1% longer than in ice-*Ih*) but instead involves distortion of the O-O-O angles. The angles in ice-*Ih* (109°) are close to the ideal tetrahedral value [3], whereas in MH-III they range between 90° and 120°. While these differ considerably from the ideal value they are consistent with the range of values found in the high-pressure phases of ice—for example, ice-II exhibits a very similar range of angles [3]. This tendency to respond to perturbation by a change of the angles rather than of the O...O distances appears to be the general response of water networks. Densification up to 2 GPa through the various phases of ice is also achieved largely by distortion of

O-O-O angles [3]. However, in MH-III, the distortion of the angles from ideal tetrahedral values produces a water network which is 15% *less* dense than ice-*Ih* at atmospheric pressure [24]. Nevertheless, the overall density of MH-III is within $\sim 1.0\%$ of the mean density of a 2:1 mixture of ice-VII and methane-I at 3.0 GPa [22,26]. Since both ice-VII and methane-I have densely packed structures—methane-I is close packed [22] and ice-VII undergoes no coordination changes up to at least 150 GPa [27]—it appears that MH-III is also densely packed and may be stable over a pressure range much wider than the current observed range of ~ 10 GPa [16].

The C \cdots O contact distances reveal that the methane-water repulsions in MH-III are quite strong. Whereas the long C \cdots O distances of ~ 3.8 Å found in MH-I lie close to the minimum in the methane-water potential as shown in Fig. 1 of Ref. [28], the C \cdots O distances of ~ 3.3 Å in MH-III lie well into the repulsive part, with a repulsive interaction energy of the order of ~ 1 kJ mol $^{-1}$ [28] at 3.0 GPa. MH-III thus provides experimental access to a completely unexplored regime of the methane-water interaction [5] and will prove to be a valuable system for studies of dynamics and modeling to improve knowledge of this part of the potential. The repulsive interaction increases strongly with pressure and is more than doubled at 11 GPa (the highest pressure reached in this study), where the C \cdots O distances are reduced to ~ 3.1 Å. It is clearly now of great interest to explore this system to much higher pressures, both to probe deeper into the repulsive region and to establish the ultimate stability limit of the MH-III structure.

In spite of the relatively large distortions of its water network, MH-III has key structural features in common with the filled-ice gas hydrates [8,9]. Like these structures, MH-III in no sense has cages, and instead the guest molecules sit in channels within the water network with relatively short ~ 3.3 Å water-guest distances. MH-III can thus be regarded as a filled ice. It is the first to be found with an ice-*Ih*-related water network, and the first example of a transformation from a cage clathrate to a filled ice. Many other cage clathrates have been shown to have phase transitions in the 1–2 GPa range [10–14] and it is probable that these transitions also signal a change from cage structures to channel or filled ice structures. It is likely that this type of transformation provides a route by which stable gas hydrates can exist at pressures above 10 GPa [16]. However, existing evidence suggests that the structures are not the same in detail as methane hydrate and these differences are likely to be determined by the repulsive part of the gas-water potentials now being opened up to study.

We thank S. A. Belmonte, D. R. Allan, and D. J. Francis for assistance with experiments and Y. P. Handa for sample preparation. This work is funded by the U.K. EPSRC and supported by the U.K. CLRC through access to beam time at ISIS and SRS, and other resources. We also acknowledge support from the British Council.

- [1] H. Davy, Philos. Trans. R. Soc. London **101**, 1 (1811).
- [2] G. A. Jeffery, Compr. Supramol. Chem. **8**, 788 (1984).
- [3] V. F. Petrenko and R. W. Whitworth, *Physics of Ice* (Oxford University Press, Oxford, 1999), Chap. 11, pp. 252–283.
- [4] G. Hummer, S. Garde, A. E. Garcia, M. E. Paulaitis, and L. R. Pratt, Proc. Natl. Acad. Sci. U.S.A. **95**, 1552 (1998).
- [5] K. Lum, D. Chandler, and J. D. Weeks, J. Phys. Chem. B **103**, 4570 (1999).
- [6] W. S. Holbrook, H. Hoskins, W. T. Wood, R. A. Stephen, and D. Lizarralde, Science **273**, 1840 (1996).
- [7] J. I. Lunine and D. J. Stevenson, Icarus **70**, 61 (1987).
- [8] W. L. Vos, L. W. Finger, R. J. Hemley, and H. K. Mao, Phys. Rev. Lett. **71**, 3150 (1993).
- [9] D. Londono, J. L. Finney, and W. F. Kuhs, J. Chem. Phys. **97**, 547 (1992).
- [10] Y. A. Dyadin, E. G. Larionov, D. S. Mirinski, T. V. Mikina, and L. I. Starostina, Mendeleev Commun. **7**, 32 (1997).
- [11] Y. A. Dyadin, E. Y. Aladko, and E. G. Larionov, Mendeleev Commun. **7**, 34 (1997).
- [12] Y. A. Dyadin, E. G. Larionov, A. Y. Manakov, F. V. Zhurko, E. Y. Aladko, T. V. Mikina, and V. Y. Komarov, Mendeleev Commun. **9**, 209 (1999).
- [13] M. G. E. van Hinsberg, M. I. M. Scheerboom, and J. A. Schouten, J. Chem. Phys. **99**, 752 (1993).
- [14] H. T. Lotz and J. A. Schouten, J. Chem. Phys. **111**, 10242 (1999).
- [15] C. Gutt, B. Asmussen, W. Press, M. R. Johnson, Y. P. Handa, and J. S. Tse, J. Chem. Phys. **113**, 4713 (2000).
- [16] J. S. Loveday, R. J. Nelmes, M. Guthrie, S. A. Belmonte, D. R. Allan, D. D. Klug, J. S. Tse, and Y. P. Handa, Nature (London) **410**, 661 (2001).
- [17] Deuteration eliminates the high background given by incoherent neutron scattering from hydrogen atoms.
- [18] Y. P. Handa, J. Chem. Thermodyn. **18**, 915 (1986).
- [19] J. M. Besson, R. J. Nelmes, G. Hamel, J. S. Loveday, G. Weill, and S. Hull, Physica (Amsterdam) **180B–181B**, 90 (1992).
- [20] R. J. Nelmes, J. S. Loveday, R. M. Wilson, J. M. Besson, S. Klotz, G. Hamel, and S. Hull, Trans. Am. Crystallogr. Assoc. **29**, 19 (1993).
- [21] R. J. Nelmes and M. I. McMahon, J. Synchrotron. Radiat. **1**, 69 (1994).
- [22] R. M. Hazen, H. K. Mao, L. W. Finger, and P. M. Bell, Appl. Phys. Lett. **37**, 289 (1980).
- [23] The refined values of the variable structural parameters at 3.0(1) GPa, were $a = 4.7458(5)$ Å, $b = 8.0644(9)$ Å, $c = 7.8453(7)$ Å, $y(\text{C}) = -0.1857(15)$, $U_{\text{iso}}(\text{C}) = 2.9(10) \times 10^{-2}$ Å 2 , $y(\text{O}) = 0.4100(10)$, $z(\text{O}) = 0.1792(6)$, $U_{\text{iso}}(\text{O}) = 1.0(4) \times 10^{-2}$ Å 2 . $x(\text{C}) = 1/4$, $z(\text{C}) = 0$, and $x(\text{O}) = 1/4$. (There is a 0, 1/4, 0 shift of origin compared with the 1/4, 0, 0 *I2bm* sites mentioned in the text.)
- [24] V. F. Petrenko and R. W. Whitworth, *Physics of Ice* (Ref. [3]), Chap. 2, pp. 10–35.
- [25] G. A. Jeffrey, *An Introduction to Hydrogen Bonding* (Oxford University Press, Oxford, 1997).
- [26] R. J. Hemley, A. P. Jephcoat, H. K. Mao, C. S. Zha, L. W. Finger, and D. E. Cox, Nature (London) **330**, 737 (1987).
- [27] P. Loubeyre, R. LeToullec, E. Wolanin, M. Hanfland, and D. Hausermann, Nature (London) **397**, 503 (1999).
- [28] J. S. Tse, M. Klein, and I. McDonald, J. Phys. Chem. **87**, 4198 (1983).