The crystal structure of methane phase III

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Methane is the simplest organic molecule, and like many supposedly simple molecular materials it has a rich phase diagram. While crystal structures could be determined for two of the solid phases, that of the low temperature phase III remained unsolved. Using high-resolution neutron powder diffraction and a direct-space Monte Carlo simulated annealing approach, this fundamental structure has now finally been solved. It is orthorhombic with space group $Cmca$, and 16 molecules in the unit cell. The structure is closely related to that of phase II, yet is no subgroup of it. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1580809]

Methane ices are fascinating fundamental solids and, analogous to water ices, have been investigated extensively over the past 60 years using a variety of experimental techniques and theoretical methods. Recently, the methane clathrates, inclusion compounds composed of both H_2O and CH_4 have attracted considerable attention.[1] Methane is the simplest organic molecule. However, the apparent simplicity of this fundamental molecule belies the structural complexity of the solid-state phase diagram. Of at least seven known phases of solid methane,[2,3] only the two cubic phases have been completely solved.[4,5] In both cases the carbon atoms in the center of the tetrahedral molecule occupy a face-centered cubic (fcc) lattice, demonstrating a tendency of the methane molecules to approximate to spheres and to form close packed crystal structures.[6] In phase I, which at ambient pressure is stable below a melting temperature of about 90 K and above $T=20.4\,\mathrm{K}\,(CH_4)$ and $T=27.0\,\mathrm{K}\,(CD_4)$, all of the tetrahedral molecules are orientationally disordered. In phase II, below these temperatures, the orientation-dependent octupole–octupole interaction leads to partial orientational order. The crystal structure is described in the spacegroup $Fm3c$, with six orientationally ordered sublattices and two disordered sublattices. It is sometimes referred to as ''antiferrorotational.''[4,5]

The existence of phase III of solid methane has been known for more than 60 years.[7] For CD_4 it is the stable phase below 22.1 K, while for CH_4 moderate pressure ($\geqslant$200 bar) is required in addition to low temperature in order to stabilize the phase. An extensive literature regarding excitations in phase III is available. However, knowledge of the crystal structure is a prerequisite for the full understanding and interpretation of the experimental data. By far the most complete theoretical analysis of the phase III structure has been performed by Maki *et al.*[8] The original approach of James and Keenan[5] is restricted to the interaction of electrostatic octupole moments, the lowest order moment of the methane molecule. Maki *et al.* add a crystal field term (which goes beyond electrostatics) which only depends on the orientation of the molecule considered. As the analysis is done on a rigid face-centered cubic center of mass (c.o.m.) lattice, to leading order, the crystal field acts on the hexadecapole moments of the molecules. With this extended James and Keenan model, they suggest the tetragonal space group $P4_2/mbc$ as the most stable low temperature structure.

Despite strenuous efforts, the crystal structure of CD_4-III has remained unsolved for a number of reasons. In retrospect, three major obstacles to structure solution can be identified: (1) It is extremely difficult to grow powder samples of sufficient quality and it is virtually impossible to grow single crystals of phase III. (2) A pseudosymmetric cell obscured the determination of the correct space group. With the knowledge of the structure presented here, it is now clear that previous published and unpublished efforts using diffraction—from Gissler[9] and Arzi[10] to Press[11] and Prokhvatilov[12]—had little chance to solve the problem. (3) Software for crystal structure solution from powder diffraction data by direct-space methods was not readily available.

Prompted by the fundamental nature of methane, and the high current level of interest in the complex phase behavior of such simple molecules in the crystalline phase,[13] we have tackled the methane phase III problem once again, this time using very high-resolution neutron powder diffraction. With improved *in situ* crystallization techniques, and the ability of neutron diffraction to provide full structural information including the positions of H(D) atoms, we aimed to produce a

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definitive description of the structure of CD_4-III.

In this latest attempt, neutron powder diffraction data from solid CD_4 were recorded using the high-resolution neutron diffractometer (HRPD) at the pulsed spallation source ISIS, Rutherford Appleton Laboratory, UK. HRPD utilizes the time-of-flight method and offers a constant resolution $\Delta d/d$ of some 0.05%. Special care was taken to produce a high-quality powder sample, that had to be of high crystallinity and strain-free with as little preferred orientation as possible. Instead of crystallizing the sample from the liquid phase at the melting temperature, which inevitably gives rise to large crystallites condensation from the gas phase at about 7 K was used to produce a nanocrystalline methane snow. After this ''shock-therapy'' careful annealing at temperatures around 50–60 K led to polycrystalline samples very close to the desired quality. The procedure is not straightforward. Short annealing at relatively low temperature yields very good sample isotropy but very small crystallites broaden the Bragg peaks, negating the high instrumental resolution. On the other hand, long annealing at high temperatures gives rise to large crystallites and sharp diffraction peaks, but inevitably leads to pronounced preferred orientation. A compromise had to be found on the instrument by monitoring the size of crystallites via the width of the Bragg peaks. In the present instance, the crystallinity of the sample, with a volume of 2 cm^3, results in a resolution $\Delta d/d$ of 0.22% with a scatter of intensities due to preferred orientation effects of approximately 10%.[14] The amount of preferred orientation of the sample was initially estimated from refinements with independent data sets of CD_4-I and CD_4-II, obtained from the same sample. CD_4-III data were recorded at $T=18$ K, only slightly below the phase II–III transition at 22.1 K, and covered a d-spacing range of 0.83–3.67 Å.

It was already known from earlier work that the phase III diffraction pattern has a certain similarity with that of phase II.[4] Apparently, the C atoms in the center of the methane molecules comprise a lattice close to a face-centered cubic structure and correspondingly a relation with the orientational order of phase II is suggested. Furthermore, high-resolution inelastic neutron scattering experiments indicate the absence of quantum mechanically free rotation. Instead, a relatively large number of tunneling lines is observed,[15–17] which can be related to the onset of complete orientational order in phase III. A very good fit of this observed tunneling multiplet is obtained using a two-site model with either mirror planes at both molecular sites or a twofold axis at one and a mirror plane at the other[15–17] which is in agreement with the structure proposed in the following. The well documented first-order nature of the II–III transition puts a group–subgroup relation in question.

An initial analysis of our neutron data suggested a tetragonal primitive cell with $c=11.708$ Å and $a=b=8.187$ Å (this effectively corresponds to a 1.0% tetragonal distortion of the original cubic structure), containing 16 molecules per unit cell. The structure within space group $P4_2/mbc$, as suggested by Maki *et al.*[8] was not in agreement with the neutron powder data. There also was no convergence when fitting the diffraction profiles with models using selected tetragonal space groups of high symmetry and in accordance with the observed extinctions. After further failures to fit the data on the basis of the three low symmetry tetragonal space groups $P4$, $P4_2$, $P\bar{4}$ a more radical approach was taken.

The state-of-the-art software package Reflex Plus[18] was used, which is based on the Powder Solve approach.[19] Guided by a Monte Carlo simulated annealing algorithm, large numbers of trial structures are generated. A powder diffraction pattern is calculated for each trial structure and compared to the experimental data. The goal of the procedure is to find the global minimum of the weighted Rietveld parameter R_{wp} that measures the agreement between the calculated and experimental powder pattern.

Structure solution was attempted in the 29 tetragonal space groups that can account for all experimentally observed Bragg peaks. Assuming a nearly face-centered cubic arrangement of localized molecules, all possibilities of placing molecules on special positions were explicitly taken into account. Each molecule in the asymmetric unit was defined as a rigid body. After discarding all tetragonal space groups, the search was extended to the orthorhombic crystal system and the structure was finally solved in $Cmca$, one of the two orthorhombic space groups that are in best agreement with the observed systematic absences. The lattice constants were found to be $a=11.7079(1)$ Å, $b=8.1893(1)$ Å, and $c=8.1842(1)$ Å, the small splitting of 0.06% of the cell parameters b and c being difficult to detect from the available experimental data. The numbers in brackets denote the error which is in the 0.001% range. Our success in achieving the crystal structure solution of phase III of methane is the result of a systematic search in a large number of space groups. The ability to carry out such a search is closely linked to the use of a novel, fast and easy-to-use software tool.

The phase III structure within the space group $Cmca$ has 16 molecules in the unit-cell. Half of the molecules lie on mirror planes perpendicular to the a axis at $x=0$ and $x=a/2$ (sites A), while the other eight molecules occupy positions on twofold axes parallel to the a axis at $x\simeq a/4$ and $x\simeq 3a/4$ (sites B). As expected, the carbon atoms in the center of the CD_4 tetrahedra adopt a nearly face-centered cubic arrangement.

The Rietveld package GSAS[20] was used to perform the final structure refinement. Treating all molecules as rigid bodies, $R_{wp}=3.9\%$ was obtained with 24 structural parameters and 31 profile parameters (Fig. 1), which improved to $R_{wp}=3.4\%$ when dropping the rigid body condition. There is virtually no departure of the c.o.m. of the molecules from the ideal fcc positions on sites A, while the displacement for molecules located on sites B are relatively large (~0.18 Å, see Table I).

More dramatic effects concern the orientational order in phase III (Fig. 2), though a relation with that of phase II remains. Taking the mirror plane at $x=0$ as reference, the molecules in this plane have similar orientations as in phase II, while those on the mirror plane at $x=a/2$ are flipped by an angle of about 90°. The departure from the high symmetry orientation of phase II ($4m2$) is $\pm 4.5°$. In the planes at $x\simeq a/4$ and $x\simeq 3a/4$ the molecules already ordered in phase II remain close to their original positions and orientations, with

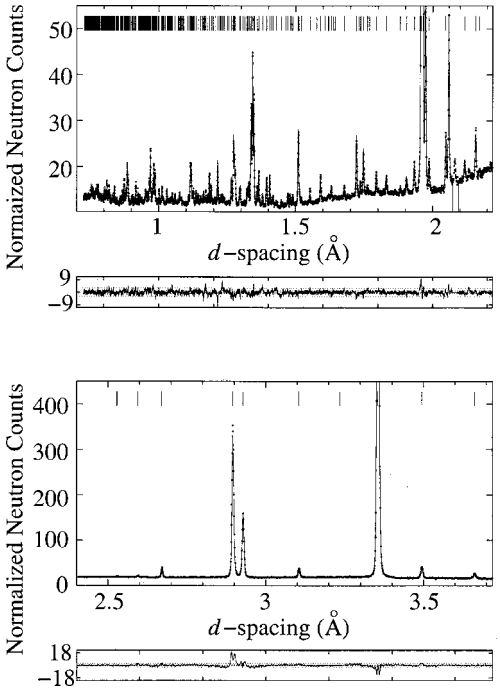

FIG. 1. Section of the observed (points) and calculated (line) neutron powder diffraction profiles of CD_4-III at $T=18$ K. The lower trace represents the difference between observed and calculated intensities divided by the estimated standard deviation. Vertical tick marks represent the calculated positions of the Bragg peaks.

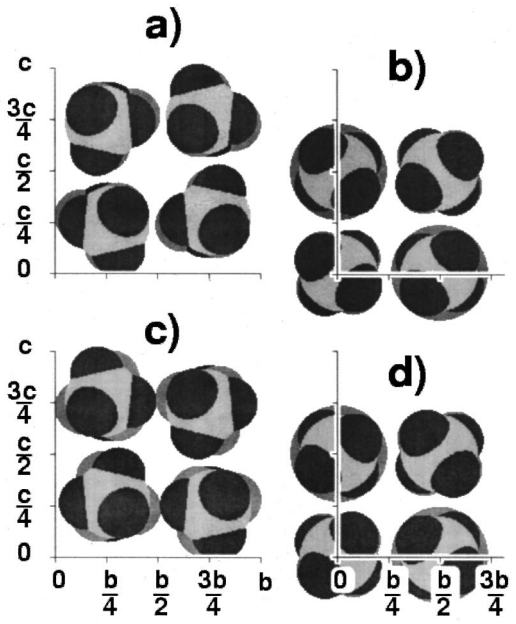

FIG. 2. Arrangement of the methane molecules in phase III of CD_4. Phase II is shown as reference (in gray behind molecules representing phase III). In the plane at $x=0$ (a), only small rotations and translations, the latter within the plane, occur. As can be seen, the translation is the major effect. The site symmetry at the molecular c.o.m. is $m(100)$. In the plane at $x \approx a/4$ (b) the most important effect at the II−>III phase transition is the ordering of the previously disordered molecules, which are depicted as large spheres. Furthermore there is a small rotation of the other molecules around an axis perpendicular to the plane and an out of plane translation. The site symmetry at the molecular c.o.m. is 2(100). The other important change with respect to phase II is a reorientation of methane molecules in the planes at $x=0$ and $x=a/2$. (c). The molecules rotate about 90° within the plane. Apart from this flip small translations within the plane occur. In phase III the two planes are connected by the translation $+(1/2\ 1/2\ 0)$ which does not exist in phase II. The planes at $x \approx a/4$ and at $x \approx 3a/4$ (d) are connected in the same way. The symmetry operation now relates ordered and disordered molecules of phase II.

a change of orientation by 5.2° (Table I). The formerly disordered molecules order. At all sites the librational amplitudes are about 15° half width at half maximum. In summary, 8 of the 16 molecules in the unit cell hardly change their orientation, 4 flip by about 90°, and 4 order orientationally. Evidently, there cannot be a group–subgroup relationship between the structures of phase II and phase III.

While the ordering of the molecules in the planes perpendicular to the *a* axis is very reminiscent of that in phase II, the stacking along the *a* axis is different and energetically less favorable as can be concluded from the lattice expansion along this direction. Obviously complete orientational order of tetrahedra on a fcc lattice is connected with frustration effects.

TABLE I. Coordinates of atoms at the A (twofold axis) and B (mirror-plane) sites in phase III of solid methane, as determined from a rigid body refinement of tetrahedral molecules (rigid with symmetry—43 m) using GSAS (Ref. 19). In order to facilitate the use of the table and also for unambiguity, the coordinates of D atoms not related by symmetry are given, too ($D12_A$, $D22_B$, $D23_B$). For the atomic displacements U_i in Å, only average quantities are presented.

	X	*Y*	*Z*	$U_i \times 100$
C_A	0.7498(2)	0.5	1.0	3.0(1)
$D11_A$	0.8010(3)	0.5795(2)	0.9336(2)	8.8(3)
$D12_A$	0.6986	0.5663	1.0796	8.8
C_B	0.0	0.7296(2)	0.2303(2)	3.3(1)
$D21_B$	0.0	0.6059(3)	0.1992(4)	8.2(3)
$D22_B$	0.0	0.7416	0.3574	8.2
$D23_B$	0.0728	0.7855	0.1823	8.2

When the temperature is lowered with the passage from phase I to phase III the interaction energy gradually defeats entropic effects. As a consequence, the molecules are observed to undergo transitions from complete orientational disorder (phase I) to partial order (phase II) and, finally, to complete order in phase III. Details of the interaction become important, and lead to lower symmetry, thus removing the symmetry of the phase II structure. Details of the c.o.m. arrangement probably are important for minimizing the free energy in phase III. In our opinion, Maki *et al.*[8] did not succeed with their calculation because it was based on an unperturbed c.o.m. lattice and they only considered subgroups of the phase III structure.

Application of this new structural knowledge will enable a better theoretical understanding of CD_4-III to be obtained. Lattice energy calculations will provide a stringent test of what is known about interactions in solid methane.[21] The crystal structure of phase III will challenge the understanding of the interaction at low temperature and close to normal pressure. In addition, its solution will enable the full analysis of a considerable amount of experimental data of a compound that has been thought to be the ''simplest'' organic solid. For example, the tunneling spectra can now be ex-

plained fully.[22] Earlier neutron tunneling spectroscopy, as outlined in Ref. 16, was rather close to finding the correct structure in also pointing to a two-sublattice structure with appropriate site symmetries. In addition, there is a host of optical spectroscopic data[23–27] also used to identify the phase III structure. Revisiting these publications leads to the conclusion that a derivation of the correct space group from all these data seems impossible, while there is no contradiction to the results of a factor group analysis (which allows more peaks than actually observed: peak intensities may be too weak and also there may be degeneracies). Methane is known to occur in planetary environments and it is hoped that this work will reinvigorate investigations of the high-pressure structures[28,29] of solid methane. High pressure is thought to render the effect of the crystal field more important as compared to the orientation dependent interaction. Apparently, at high pressures there is a transition from perturbed fcc to perturbed hcp structures. It has been predicted, and in the meantime observed, that methane dissociates at very high pressures.[30] The approach presented in this paper is generally applicable to the structure elucidation of the various solid phases of other small molecules.

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[1] J. S. Loveday, R. J. Nelmes, M. Guthrie, D. D. Klug, and J. S. Tse, Phys. Rev. Lett. **87**, 215501 (2001).
[2] R. Bini and G. Pratesi, Phys. Rev. B **55**, 14800 (1997).
[3] R. Bini, L. Ulivi, H. J. Jodl, and P. R. Salvi, J. Chem. Phys. **103**, 1353 (1995).
[4] W. Press, J. Chem. Phys. **56**, 2597 (1972).
[5] H. M. James and T. A. Keenan, J. Chem. Phys. **31**, 12 (1959).
[6] H. H. Mooy, Nature (London) **127**, 707 (1931).
[7] K. Clusius, L. Popp, and A. Frank, Physica IV **10**, 1105 (1937).
[8] K. Maki, Y. Kataoka, and T. Yamamoto, J. Chem. Phys. **70**, 655 (1979).
[9] W. Gissler and H. H. Stiller, Naturwissenschaften **52**, 512 (1965).
[10] E. Arzi and E. Sandor, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **31**, 188 (1975).
[11] W. Press and A. Hüller, *Anharmonic Lattices, Structural Transitions and Melting*, edited by T. Riste (Noordhoft, Leiden, 1979), pp. 185–212.
[12] A. I. Prokhvatilov and A. P. Isakina, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **36**, 1576 (1980).
[13] R. Hemley, Annu. Rev. Phys. Chem. **51**, 763 (2000).
[14] For x rays the problem is even more severe because of the smaller volume; in this case image plates appear obligatory as the detector unit in order to visualize and understand the preferred orientation via the ''graininess'' of the Debye–Scherrer rings.
[15] M. Prager, W. Press, and A. Heidemann, J. Chem. Phys. **75**, 1442 (1981).
[16] M. Prager, W. Press, A. Heidemann, and C. Vettier, J. Chem. Phys. **77**, 2577 (1982).
[17] M. Prager and W. Press, J. Chem. Phys. **92**, 5517 (1990).
[18] Reflex Plus, Accelrys Inc., 9685 Scranton Road, San Diego, CA 92121-3752.
[19] G. E. Engel, S. Wilke, O. König, K. D. M. Harris, and F. J. J. Leusen, J. Appl. Crystallogr. **32**, 1169 (1999).
[20] A. C. Larson and R. B. Von Dreele, GSAS—The general structure analysis system, Los Alamos National Laboratory, Los Alamos, NM 87545, 1985.
[21] T. Yamamoto and Y. Kataoka, Phys. Rev. Lett. **20**, 1 (1968).
[22] M. Prager, W. Press, B. Asmussen, and J. Combet, Appl. Phys. A: Mater. Sci. Process. **74**, S1360 (2002); J. Chem. Phys. **117**, 5821 (2002).
[23] C. Chapados and A. Cabana, Chem. Phys. Lett. **7**, 191 (1970).
[24] B. W. Baran and F. D. Medina, Chem. Phys. Lett. **129**, 125 (1986); **176**, 509 (1991).
[25] P. Calvani and S. Lupi, J. Chem. Phys. **90**, 5924 (1989).
[26] D. Fabre, M. M. Thiéry, H. Vu, and K. Kobashi, J. Chem. Phys. **71**, 3081 (1979).
[27] F. D. Medina and W. B. Daniels, J. Chem. Phys. **70**, 242 (1979); F. D. Medina and W. B. Daniels, *ibid.* **70**, 2688 (1979).
[28] I. Nakahata, N. Matsui, Y. Akahama, and H. Kawamura, Chem. Phys. Lett. **302**, 359 (1999).
[29] J. S. Loveday, R. J. Nelmes, W. G. Marshall, J. M. Besson, S. Klotz, and G. Hamel, Physica B **241–243**, 240 (1998).
[30] L. R. Benedetti, J. H. Nguyen, W. A. Caldwell, H. Liu, M. Kruger, and R. Jeanloz, Science **286**, 100 (1999).