

Structural studies of solid methane at high pressures

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Abstract

High-pressure X-ray powder diffraction measurements for solid methane were performed at pressures up to 13 GPa. The diffraction pattern at 7.0 GPa is assigned to a rhombohedral lattice with lattice constants of $a = 8.643(1)$ Å and $\alpha = 89.40(2)^\circ$ and with a unit cell that contains 21 molecules. The bulk modulus of the rhombohedral phase is estimated to be 7.9(3) GPa. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Methane is the simplest of the saturated hydrocarbon compounds and is an important constituent of the solar system. Solid methane exhibits several crystalline phases based mainly on the difference in the orientation of molecules in the unit cell. Many optical studies have been performed in the past to investigate the phase diagram of solid methane [1–9]. Bini and co-workers [1,2] recently proposed the phase diagram shown in Fig. 1. In the diagram, there are only two phases whose crystal structures have been determined by an X-ray diffraction analysis. Phase I has an fcc structure (Fm3m) with one freely rotating molecule in the unit cell [10]. Phase II is also an fcc (Fm3c) and contains eight molecules, of which six are orientationally ordered and the other two behave as weakly hindered rotators in the unit cell [11]. For the other phases in Fig. 1, only crystal symmetries are assumed based on optical measurements.

Under isothermal compression at 300 K, methane crystallizes into phase I at ~ 1.6 GPa. With further increasing pressure, the transition to phase A takes place at 5.25 GPa. Hazen et al. pointed out that this transition takes place reversibly and rapidly and the molecules are rearranged by the transition [10]. Bini and Pratesi have inferred from optical measurements that phase A might have a tetragonal cell [1].

In this Letter, we report the results of powder X-ray diffraction experiments for phase A of solid methane.

2. Experimental

A diamond anvil cell (DAC) with a cone-shaped aperture to detect diffraction X-rays was used for high pressure generation. Gaseous CH_4 was obtained from Liquid-Gas Co. Ltd. Its stated purity was ~ 99.9999 vol%. It was sprayed on the metal gasket (U-700) fixed on a lower anvil in the DAC, which was cooled by liquid nitrogen in a dry box. The pressure was quickly applied up to ~ 5 GPa at low temperature to prevent crystal growth. The pressure

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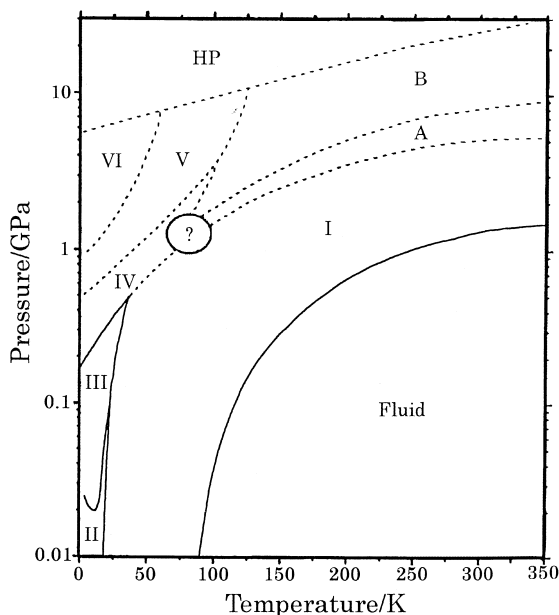


Fig. 1. Phase diagram of solid methane proposed by Bini and co-workers [1,2]. The solid lines indicate the phase boundaries characterized before Bini and co-workers. The dashed lines are the phase boundaries proposed by them. The area marked with a question mark represents a region where the phase boundaries have not been determined.

was determined by the ruby fluorescence method. An X-ray diffraction experiment at room temperature was carried out with a synchrotron radiation source on the beam line BL10XU at SPring-8. The wavelength was tuned with a Si(111) double-crystal monochromator to 0.4373 Å. Powder patterns were obtained by an angle-dispersive method with an image plate (IP) detector. The obtained diffraction images were analyzed using an integration software named the Powder Pattern Analyzer for an Imaging Plate (PIP) by Fujihisa and co-workers [12].

3. Results and discussion

Fig. 2 shows the X-ray diffraction profiles for solid methane at pressures of 7.0 and 12.9 GPa. The pattern at 7.0 GPa is assigned to a rhombohedral lattice with lattice constants of $a = 8.643(1)$ Å and $\alpha = 89.40^\circ$. This structure is similar to phase I of CF_4 (plastic phase, $a = 11.58$ Å, $\alpha = 89.49^\circ$ at 80 K) [13] and phase Ib of CCl_4 ($a = 14.41$ Å, $\alpha = 89.46^\circ$, $Z = 21$) [14]. The observed and calculated d -values are listed in Table 1. With increasing pressure at

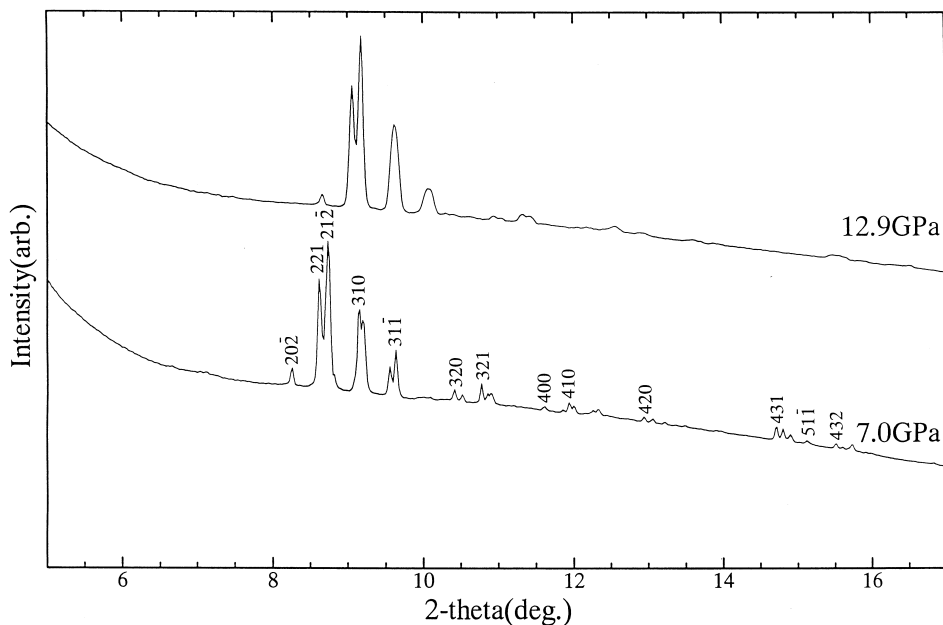


Fig. 2. Diffraction patterns of solid methane at pressures of 7.0 and 12.9 GPa. The patterns are assigned to the rhombohedral lattice with lattice constants of $a = 8.643(1)$ Å and $\alpha = 89.40(2)^\circ$ for the lower panel and $a = 8.231(1)$ Å and $\alpha = 89.44(3)^\circ$ for the upper one.

Table 1

Observed and calculated d -values of phase A at 7.0 GPa and room temperature

hkl	$2\theta_{\text{obs.}}$ (°)	$d_{\text{obs.}}$	$d_{\text{calc.}}$
20 $\bar{2}$	8.254	3.038	3.040
221	8.625	2.908	2.908
21 $\bar{2}$	8.744	2.868	2.867
310	9.156	2.739	2.741
30 $\bar{1}$	9.205	2.725	2.724
311	9.563	2.623	2.623
31 $\bar{1}$	9.639	2.602	2.603
320	10.418	2.408	2.408
30 $\bar{2}$	10.518	2.385	2.385
321	10.781	2.328	2.329
32 $\bar{1}$	10.873	2.308	2.311
31 $\bar{2}$	10.902	2.302	2.301
400	11.615	2.161	2.160
322	11.856	2.117	2.117
410	11.947	2.101	2.101
32 $\bar{2}$, 40 $\bar{1}$	12.004	2.091	2.091
330, 411	12.260	2.048	2.048
41 $\bar{1}$	12.332	2.036	2.036
420	12.943	1.940	1.940
40 $\bar{2}$	13.054	1.924	1.924
421	13.214	1.900	1.899
41 $\bar{2}$	13.343	1.882	1.880
332	13.485	1.862	1.861
431	14.710	1.708	1.708
43 $\bar{1}$, 510	14.799	1.698	1.698
41 $\bar{3}$	14.900	1.686	1.686
511	15.019	1.673	1.670
51 $\bar{1}$	15.119	1.662	1.662
432	15.511	1.620	1.620
520	15.599	1.611	1.611
42 $\bar{3}$, 50 $\bar{2}$	15.727	1.598	1.599
51 $\bar{3}$	17.293	1.454	1.455
42 $\bar{4}$	17.536	1.434	1.434

Lattice constants are $a = 8.643(1)$ Å and $\alpha = 89.40(2)^\circ$.

room temperature, the pattern did not appreciably change without the smearing out of some diffraction peaks due to the increasing peak width (the upper panel in Fig. 1). The d -values of all lines exhibit smooth changes and the relative intensities of the reflections remain almost constant up to 12.9 GPa. These results indicate that the rhombohedral lattice is still retained. This is compatible with previous reports, in which the A–B transition has been described to be very sluggish and to have a large

hysteresis [1–3]. We believe that the nonhydrostatic effect is responsible for the broadening of diffraction peaks. The diffraction profiles obtained at pressures from 7.0 to 12.9 GPa should be from phase A of the solid methane. Phase A is expected to contain 21 molecules in the unit cell due to its similarity with phase Ib of CCl_4 . The lattice constants of phase A at room temperature are listed in Table 2. The rhombohedral angles were scarcely changed by the pressure within experimental accuracy.

The pressure–volume data of phase A are plotted in Fig. 3, along with a fit to the Birch–Murnaghan equation of state:

$$P = \frac{2}{3} K_0 \left[\left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right] \times \left\{ 1 - \frac{3}{4} (4 - K'_0) \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right] \right\},$$

where V_0 is the extrapolated value of the molecular volume at zero pressure, K_0 is the isothermal bulk modulus at zero pressure, and K'_0 is the pressure derivative of the isothermal bulk modulus evaluated at zero pressure. Phase A has the values of $K_0 = 7.9(3)$ GPa and $V_0 = 45.9(4)$ Å³ when K'_0 is fixed at 4. The pressure–volume relationship of phase I determined by Hazen et al. [10] is also plotted in Fig. 3. The volume decrease at the transition from phase I to phase A is estimated to be $\sim 1\%$. This value is reasonable since the volume change from phase Ia (disordered fcc) to phase Ib of CCl_4 is reported to be $\sim 2\%$ [14].

Table 2

Lattice constants of phase A

Pressure (GPa)	a_{R} (Å)	α (°)
7.0	8.643(1)	89.40(2)
7.7	8.579(2)	89.41(4)
8.2	8.537(1)	89.41(3)
8.9	8.4867(8)	89.43(2)
9.6	8.447(1)	89.43(3)
10.0	8.414(1)	89.45(3)
10.7	8.365(1)	89.45(3)
11.2	8.325(2)	89.47(5)
12.3	8.269(1)	89.47(3)
12.9	8.231(1)	89.44(3)

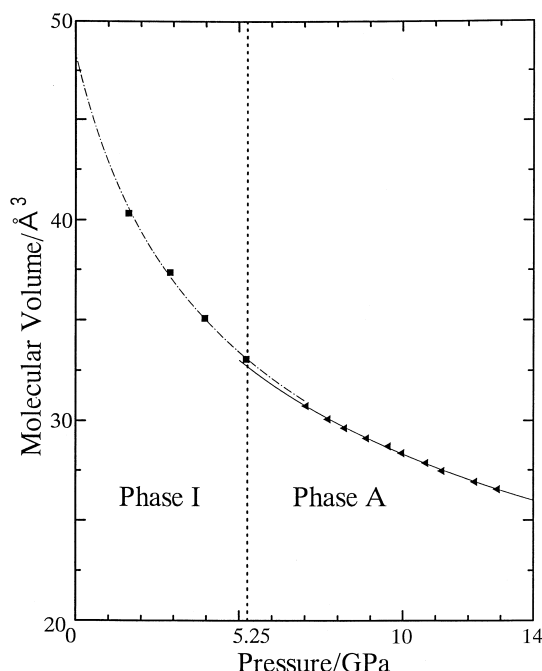


Fig. 3. Pressure dependences of molecular volume for phases A and I. The data for phase I are from Ref. [10]. The dotted line at 5.25 GPa shows the transition pressure at 293 K determined by Hazen et al. [10].

The lattice constant of phase I (fcc) at 5.21 GPa is reported to be 5.095 Å [10]. The length of a body diagonal of this cubic cell is 8.825 Å, which is slightly longer compared with the lattice constant of the rhombohedral phase A at 7.0 GPa (8.643 Å). When the rhombohedral cell is converted to a hexagonal one, the length of the *c*-axis of the converted hexagonal cell becomes 15.126 Å, which is also close to three times the lattice constant of phase I. Thus it is expected that the [111] direction of the rhombohedral lattice of phase A coincides with the [001] direction of the fcc lattice of phase I at the I–A transition. This transition, however, is not realized only by distorting the fcc lattice in one direction because the symmetry around the [111] direction of the rhombohedral lattice differs from that around the [001] direction of the fcc lattice. We can then conclude that the rearrangement of molecules takes place at the transition.

In the rhombohedral system there are seven space groups, among which five space groups ($R\bar{3}$, $R\bar{3}m$,

$R32$, $R3m$ and $R\bar{3}m$) can accommodate 21 molecules in a unit cell if the carbon atoms do not occupy C1 sites. On the other hand, Bini et al. have anticipated that the methane molecules occupy the three different sites except for the C1 site in phase A [2]. If we apply this three-site model in the rhombohedral system, methane molecules are accommodated in sites whose symmetries are not contained in the T_d symmetry of a methane molecule. We thus consider that phase A is still a disordered phase.

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