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X-ray diffraction studies and equation of state of methane at 202 GPa

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ABSTRACT

Solid methane (CH_4) was compressed up to 202 GPa at 300 K in a diamond-anvil cell. The crystal structure and equation of state over this entire range were determined from angle dispersive X-ray diffraction results. CH_4 undergoes phase transitions from rhombohedral to a simple cubic phase at 19 GPa and from simple cubic to a higher pressure cubic phase at approximately 94 GPa. This higher pressure cubic phase was stable to the maximum pressure investigated. Combined with previous optical measurements, it was found that at room temperature compressed CH_4 remains an insulator with cubic structure to 202 GPa.
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Methane (CH_4) is an abundant molecular species in the gas–ice giants, such as Uranus and Neptune [1,2], where the interior pressures reach 600–800 GPa [3,4]. High-pressure study of the properties of CH_4 is of critical importance for improved understanding of the physics and chemistry of planetary interiors and the origin of their magnetic field distribution. CH_4 has a very rich phase diagram [5–12]. Five cryogenic solids, i.e., phases II, III, IV, V, and VI only exist below 150 K and moderate pressures. Studies at room temperature showed that fluid CH_4 solidifies into the face-centered cubic (fcc) phase I at 1.6 GPa [5]. Seven additional solid phases, i.e., phases A, pre-B, B, HP1, HP2, HP3, and X, have been identified under increasing pressures up to 288 GPa at 300 K. Previous X-ray diffraction (XRD), infrared, and Raman spectroscopic studies up to 86 GPa at 300 K [6–11] have revealed that CH_4 transforms from fcc phase I to rhombohedral phase A at 5.3 GPa, to cubic phase B at 10–18 GPa, and to another slightly different cubic phase HP above 25 GPa. In-depth XRD and Raman studies to 86 GPa further divided the cubic phase HP into three cubic phases HP1 (25–35 GPa), HP2 (35–62 GPa), and HP3 (>62 GPa), according to minor differences in XRD and Raman patterns [9]. Recent time-resolved Raman measurements by Hirai et al. [9] have also indicated an intermediate, metastable phase pre-B above 12 GPa which showed a structure close to that of phase B but rotation of molecules close to that of phase A. All five high-pressure cubic phases (pre-B, B, HP1, HP2, and HP3) have simple cubic symmetry and similar lattice parameters as a function of pressure, and are distinguishable only by the intensity variations and presence of certain diffraction peaks. They are thought to indicate the differences in the state of the molecules without fundamental changes in the crystal structure, an interpretation consistent with the optical observations.

Recently much higher pressure optical reflectivity and absorption measurements by Sun et al. found that the solid CH_4 undergoes an insulator-semiconductor transition to phase X at 288 GPa [12]. However there is no experimental report on the crystal structure and density of CH_4 above 86 GPa. Here we studied the structure of CH_4 up to 202 GPa using angle dispersive XRD and determined its equation of state; these results clarify the high-pressure crystal structure of methane at ultrahigh pressure.

High pressures were generated using a diamond-anvil cell. Diamonds with low birefringence were selected for the high-pressure XRD measurements in two separate experiments. For the first experiment, diamond anvils of 300 μm flat were used with a 100 μm diameter sample hole in a Re gasket. For the second experiment, beveled anvils of 300 μm outside diameter, 8.5° bevel angle and 100 μm inside flat [13] with a 40 μm diameter sample chamber in a Re gasket were employed for reaching beyond 200 GPa. The gas loading vessel containing the diamond-anvil cell was flushed three times at a pressure of 200 MPa with high-purity CH_4 99.99% gas. The CH_4 gas was then loaded into the gasket hole, and the sample was clamp sealed and further pressurized by applying pressure in the cell via a gear box. The initial sample sizes for the two experiments were 100 μm in diameter × 40 μm in thickness and 40 μm in diameter × 25 μm thickness. Pressure was measured using the ruby scale [14] for the first experiment from 11 to 62 GPa, and using the shift of the diamond Raman for the second ultrahigh pressure experiment from 69 to 202 GPa

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[15,16]. To improve the quality of the X-ray patterns for solid CH_4 under high pressure, a small amount of amorphous boron powder was scattered onto the gasket hole before sample loading to prevent growth of large CH_4 crystals and produce a much finer powder. The amorphous boron powder has no effect on the present CH_4 XRD study; it does not produce XRD peaks and is chemically inert with respect to CH_4.

Angle dispersive XRD experiments were performed on beamline 16-IDB at the Advanced Photon Source (APS), Argonne National Laboratory (ANL). A focused monochromatic X-ray beam with a wavelength of 0.4085(1) Å was used for all the experiments. The XRD images were collected using a MAR charge-coupled device (CCD) detector, and the XRD geometry was calibrated with CeO_2.

Fig. 1 shows selected integrated XRD patterns of CH_4 at various pressures. At 11 GPa, all peaks from the sample can be indexed well with a rhombohedral unit cell. The lattice parameters of $a_R = 8.364$ Å and $\alpha_R = 89.46°$ are consistent with previously reported values [10]. Increasing pressure to 19 GPa, the appearance of new diffraction lines in addition to those of the rhombohedral pattern is observed, indicating a phase transition. This phase is simple cubic, consistent with results from Umemoto et al. [11] and Hirai et al. [9]. The rhombohedral–cubic (A–B) transition was extremely sluggish; complete conversion was not observed until reaching 29 GPa, (Fig. 1c). No intermediate phase (Pre B) as described in Ref. [9] was found between the rhombohedral–cubic transition, indicating that the formation of the Pre B phase may be kinetically limited and depends on waiting for a long time between each pressure increment.

At higher pressure, the XRD pattern of the solid CH_4 remained in its cubic (B to HP) form up to just below 100 GPa. Fig. 1e shows XRD pattern of CH_4 at 94 GPa. New XRD peaks (211,421,433) appeared at this pressure and the peak 310 emerged at higher pressure. These peaks persisted to 202 GPa, as shown in Fig. 1e–g. Fig. 2 shows X-ray images from the CH_4 sample at pressures of 161–202 GPa. Although the relative intensities change drastically, the XRD patterns can still be indexed with the similar simple cubic unit cell. The pressure dependence of the unit cell volume for the three phases of solid methane was plotted in Fig. 3. A discontinuous change was also observed at 94 GPa. Those suggest that pressure causes the CH_4 molecules to reorient in the cubic unit cell. Here we call the high pressure phase at 94–202 GPa 'c-HP' to distinguish it from the cubic phases (B to HP3) below 94 GPa. The diamonds broke when we tried to increase pressure beyond 202 GPa.

The unit-cell parameters and volumes of the rhombohedral, simple cubic, and c-HP phases of CH_4 obtained at different pressures are presented in Table 1. The volume versus pressure data of the solid CH_4 are fit to the second order Birch–Murnaghan equation of state (BM EOS) [17]:

$$P = \frac{3}{2}B_0\left[(V/V_0)^{-7/3} - (V/V_0)^{-5/3}\right]\left[1 + \frac{3}{4}(B_0' - 4)((V/V_0)^{-2/3} - 1)\right]$$

where B_0 is the isothermal bulk modulus at zero pressure, B_0' is the pressure derivative of B_0 evaluated at zero pressure, and V/V_0 is the ratio of high-pressure volume and zero-pressure volume of the sample. The resulting parameters are listed in Table 2. When $B_0' = 4$ was fixed, we obtained $B_0 = 7.85$ GPa, $V_0 = 988.1$ (Å)^3 for the rhombohedral phase and $B_0 = 23.7$ GPa, $V_0 = 728.4$ (Å)^3 for the simple cubic phase (Table 2). The present values of B_0 and V_0 are compared with previous experimental determinations. Nakahata et al. carried out XRD on rhombohedral CH_4 up to 13 GPa in a diamond-anvil cell. Their fitted value of $B_0 = 7.9$ GPa is in very good agreement with our determination. We fit the simple cubic data

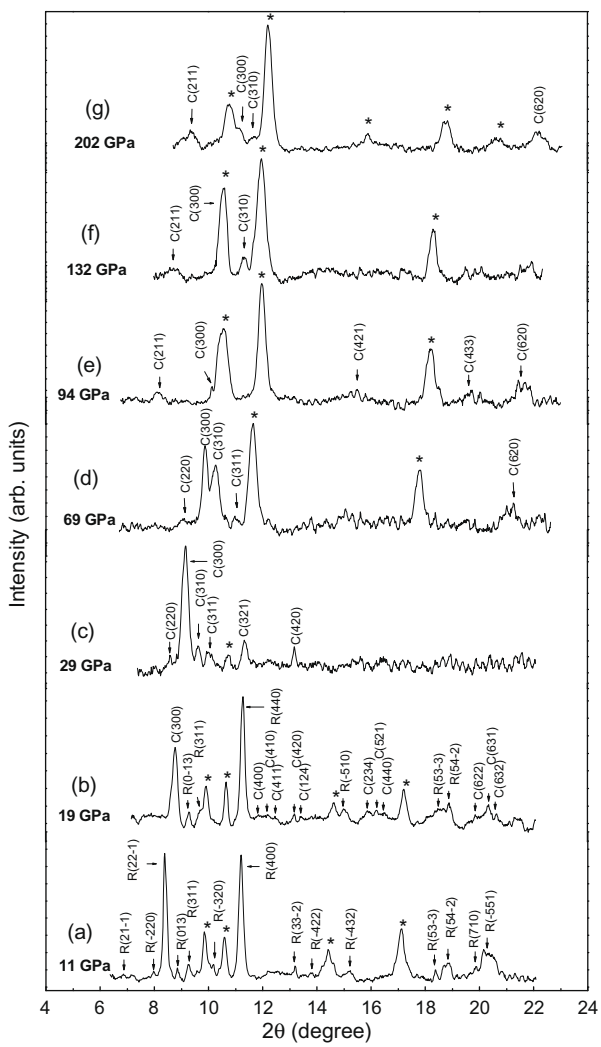

Fig. 1. Representative XRD patterns of CH_4 obtained with a monochromatic beam ($\lambda = 0.4085(1)$ Å); * indicate diffraction peaks from the Re gasket; all other labeled peaks are from the sample. (a) Rhombohedral phase at 11 GPa, (b) coexisting rhombohedral and simple cubic phases at 19 GPa, (c) and (d) the simple cubic phase at 29 and 69 GPa, (e) to (g) the high pressure c-HP phase at 94, 132 and 202 GPa.

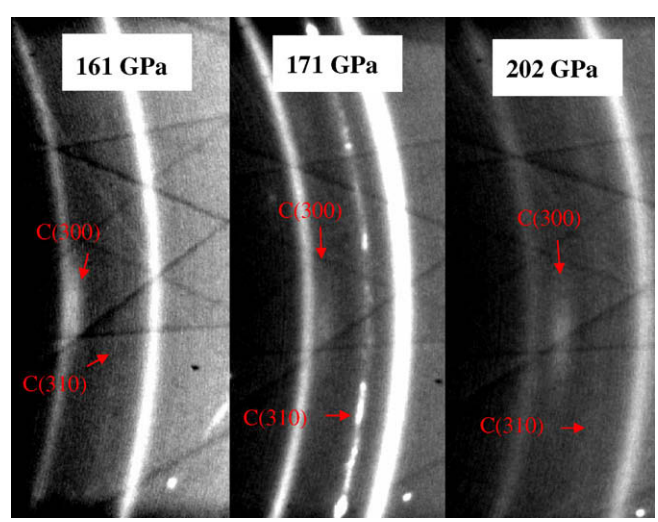

Fig. 2. X-ray images of the solid CH_4 at three pressures, showing the high pressure phase with cubic structure persisting up to 202 GPa. At high pressure the XRD from the sample became increasingly weaker. To improve the quality of XRD pattern, we reduced the X-ray focus spot size and clean-up slits at 171 GPa, and increased the exposure time for each measurement.

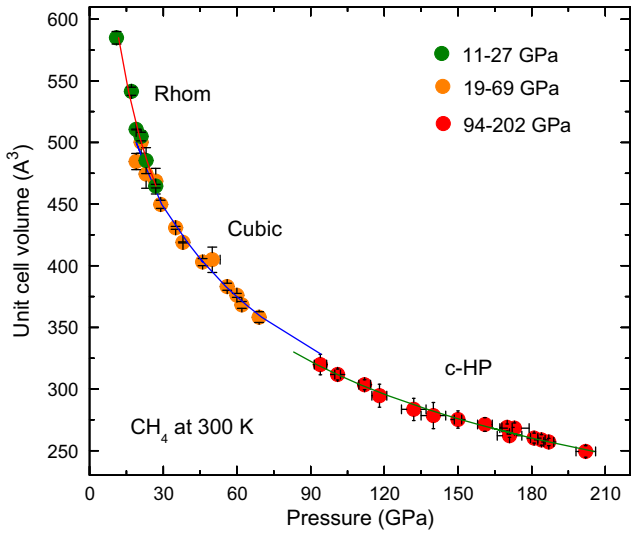

Fig. 3. Unit cell volume of different CH_4 phases as a function of pressure; solid squares, experimental data; curves, BM EOS fit to the data obtained from XRD measurements.

Table 1
Lattice parameter (a), volume (V) of three phases of solid CH_4, namely, rhombohedral (Rhom), simple cubic (SC) and high pressure phase (c-HP) obtained at different pressures (P).

P (GPa)	a_{Rhom} (Å)	V_{Rhom} (Å)	a_{SC} (Å)	V_{SC} (Å)	a_{cHP} (Å)	V_{cHP} (Å)
11	8.3632	584.95				
17	8.1507	541.48				
19	7.9924	510.55	7.8544	484.55		
21	7.9625	504.85	7.9384	500.26		
23	7.8584	485.29	7.7983	474.24		
27	7.7451	464.60	7.7674	468.63		
29			7.6617	449.75		
35			7.5522	430.75		
38			7.4821	418.86		
46			7.386	402.93		
50			7.3978	404.86		
56			7.2620	382.98		
60			7.2175	375.97		
62			7.1671	368.16		
69			7.1026	358.30		
94					6.8385	319.80
101					6.7801	311.68
112					6.7199	303.45
118					6.6536	294.56
132					6.5689	283.46
140					6.5291	278.33
150					6.5048	275.24
161					6.4724	271.14
170					6.4534	268.76
171					6.3990	262.02
173					6.4482	268.11
181					6.3842	260.21
184					6.3717	258.68
187					6.3575	256.96
202					6.2935	249.27

of Ref. [9] from 17 to 81 GPa to a BM EOS and found the resulting values of B_0 = 23.1 GPa and V_0 = 725 Å^3 in excellent agreement with our present values. The volume change at the rhombohedral to simple cubic transition is found to be $\Delta V/V = -5\%$.

We have made the first measurement of pressure–volume data for the c-HP phase of CH_4 above 94 GPa and obtained B_0 = 28.5 GPa which is slightly stiffer than the simple cubic phase. The volume change at the simple cubic to c-HP phase transition at 94 GPa is found to be $\Delta V/V = -3\%$. The constraints on volume provide the crucial information for future theoretical and experimental investigations of the microscopic behavior of CH_4 and complex molecule distribution in the unit cell.

Table 2
Bulk modulus B_0, volume extrapolated to zero pressure V_0 and pressure derivative B'_0 for three phases. Here Rhom, SC and c-HP represent rhombohedral, simple cubic and high pressure phase respectively.

P (GPa)	Phase	B_0	V_0 (Å^3)	B'_0	
11–27	Rhom	7.85 ± 0.1	988.1 ± 21	4 (fixed)	This study
7.0–13	Rhom	7.9(3)	963.9	4 (fixed	Ref. [10]
19–69	SC	23.7 ± 4.0	728.4 ± 33	4 (fixed)	This study
17–85	SC	23.1 ± 2.3	725 ± 20.3	4 (fixed)	Ref. [9]
94–202	c-HP	28.5 ± 4.6	668.3 ± 36	4 (fixed)	This study

Finally the present XRD results are consistent with previous results of optical study to megbar pressures [12]. Reflectivity and absorption measurements demonstrated that no significant changes were observed below 208 GPa, where CH_4 is an insulator. Whether a major structure transition occurs in solid CH_4 at the insulator-semiconductor transition above 288 GPa remains to be answered.

In summary, CH_4 has been studied using angle dispersive XRD to 202 GPa. CH_4 undergoes phase transformations from rhombohedral to simple cubic at 19 GPa and to a higher pressure cubic phase at 94 GPa. The equations of state for these three phases have been determined up to 202 GPa. This is the first XRD measurement of CH_4 to over 100 GPa. These types of ultrahigh pressure results have application to understanding the interiors of gas giants.

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