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X-ray diffraction measurements for solid methane at high pressures

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Abstract

X-ray powder diffraction and Raman scattering experiments for solid methane were carried out at pressures up to 37 GPa and room temperature. The diffraction pattern of phase B at 16.9 GPa is assigned to a cubic lattice with lattice constant of 7.914 Å (B). At the transition from phase B to the HP phase, the pressure–volume curve shows an anomaly without the structural change.

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. Bini and co-workers [1, 2] recently proposed the phase diagram shown in figure 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 ($Fm\bar{3}m$) with one freely rotating molecules in the unit cell [3]. Phase II is also fcc ($Fm\bar{3}c$) and contains eight molecules, of which six are orientationally ordered and the other two behave as weakly hindered rotators in the unit cell [4].

Under isothermal compression at 300 K, methane crystallizes into phase I at 1.6 GPa and the transition from phase I to A takes place at 5.25 GPa. Our previous x-ray studies clarified that phase A has a rhombohedral lattice with 21 molecules in a unit cell [5]. Under pressure higher than 5.25 GPa, phase transitions from phase A to B at 9 GPa and phase B to a high-pressure (HP) phase at 25 GPa have been revealed by optical studies [2].

In this paper, the results of x-ray powder diffraction and Raman scattering experiments for phase B and the HP phase at pressures up to 37 GPa are presented.

2. Experimental details

A diamond anvil cell (DAC) was used for high-pressure generation. The top surface of the anvils was 0.5 mm in diameter. Gaseous methane was obtained from Liquid-Gas Co. Ltd. It was sprayed on the metal gasket (U-700) fixed on a lower anvil in a DAC, which was

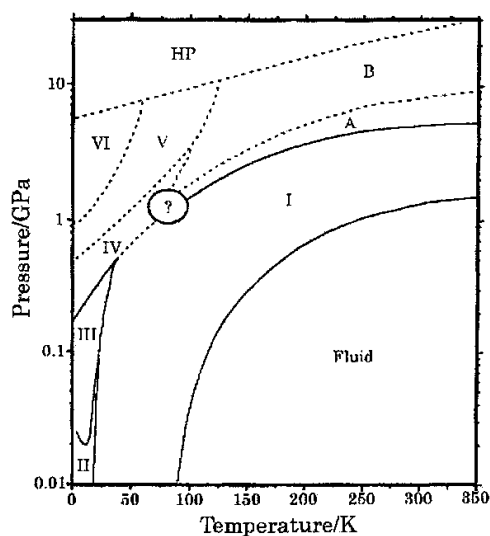


Figure 1. Phase diagram of solid methane proposed by Bini and co-workers [1, 2].

cooled by liquid nitrogen in a dry box. The pressure was quickly applied up to about 5 GPa at liquid-nitrogen temperature to prevent crystal growth. 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 0.4957 Å (B. Powder patterns were obtained by an angle-dispersive method with an image plate detector. The obtained diffraction images were analysed using an integration software package called the 'powder pattern analyser for an imaging plate' (PIP) [6]. The pressure was determined by the ruby fluorescence method [7].

High-pressure Raman spectroscopy at room temperature was carried out using a micro-optical system of a JASCO Model NR-1800 spectrometer equipped with a triple monochromator and a liquid-nitrogen cooled CCD multichannel detector. The 514.5 nm line from an Ar ion laser was used for excitation.

3. Results and discussion

Figure 2 shows the x-ray diffraction profiles for solid methane at pressures from 16.9 to 37.1 GPa. Since the transition from phase A to B is reported to be very sluggish [1, 2, 8], the transition into phase B was confirmed by the band splitting of the symmetric stretching mode (ν_1) into three peaks prior to the x-ray measurements. The diffraction pattern at 16.9 GPa is thus from phase B, which is assigned to a cubic lattice with a lattice constant of 7.914 Å (B. Phase B is expected to contain 21 molecules in a unit cell because of the reasonable dependence of molecular volume on pressure (figure 3). The volume change from phase A to B is estimated to be about 5% at 16.9 GPa.

With increasing pressure, the pattern did not change appreciably without the smearing out of some diffraction peaks due to the increasing peak width. The pattern at 37.1 GPa is still assigned to a cubic lattice. Figure 4 shows the frequency–pressure plot for the ν_1 Raman fundamental band. There is a clear discontinuity in the frequency values at around 25 GPa, which corresponds to the transition from phase B to the HP phase. The pressure–volume curve

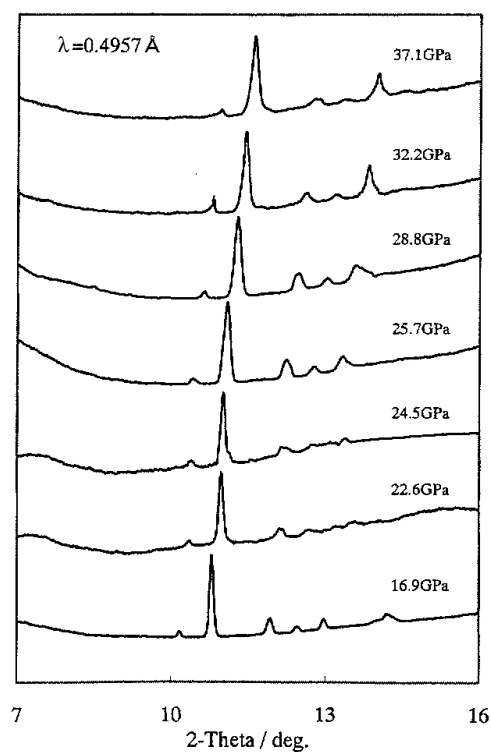


Figure 2. X-ray diffraction profiles of solid methane at pressures from 16.9 to 37.1 GPa.

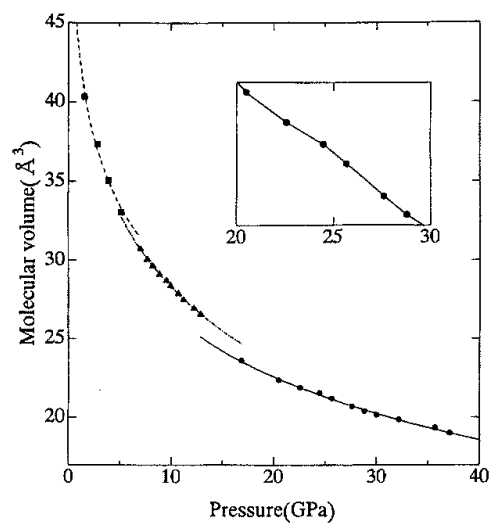


Figure 3. Pressure dependence of molecular volume for phase I (squares), A (triangles) and B (circles). The data for phase I are from [3]. The inset shows the expanded scale of the molecular volume between 20 and 30 GPa.

in figure 3 shows a slight anomaly at a pressure of around 25 GPa. The anomaly in the volume is consistent with the softening of the frequency dependence on pressure above 25 GPa.

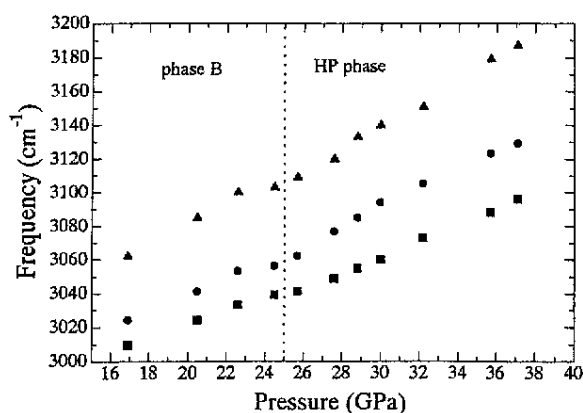


Figure 4. Frequency variation with pressure of the $n1$ components at 300 K up to 37 GPa.

Phase A has a rhombohedral structure, which is the isostructure of phase I of CF_4 and phase 1b of CCl_4 [9], and they are both plastic crystals. The post-rhombohedral phase of CF_4 and CCl_4 is an ordered monoclinic phase. Phase B is expected to be an ordered phase [1]. Nevertheless the crystal lattice of phase B is not monoclinic, but cubic. This may be due to the nearly spherical shape of methane molecules.

Acknowledgments

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