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2007 J. Phys.: Condens. Matter 19 425206

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Raman studies on solid CH₄ at room temperature to 208 GPa

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Received 3 August 2007

Published 18 September 2007

Online at stacks.iop.org/JPhysCM/19/425206

Abstract

Solid methane has been studied by Raman scattering under high pressure in a diamond anvil cell at room temperature. Internal modes ν_1 and ν_3 have been followed up to 208 GPa. The results indicated that methane remained in molecular form and kept its high-pressure phase structure to the highest pressure investigated. Fitting x-ray diffraction data from the literature by the Vinet equation of state from 16.9 to 37 GPa gives values of $K_0 = 6.4 \pm 0.73$ GPa, $K'_0 = 5.68 \pm 0.36$ and $V_0 = 25.44$ cm³ mol⁻¹. Extrapolation of the above equation of state showed that the volume of methane changes from 11.84 to 6.63 cm³ mol⁻¹ as pressure increases from 34 to 208 GPa. Furthermore, the metallization pressure of solid CH₄ has been roughly estimated on the basis of our recent results and extrapolated equation of state.

1. Introduction

The simplest hydrocarbon, methane, is a gas at room temperature and ambient pressure with a chemical formula of CH₄. Theoretical calculations by Ashcroft implied that CH₄ will become metallic at available pressures and may be a high- T_c superconductor [1]. The superconductivity of Li [2] and MgB₂ [3] also suggested that a number of compounds of low atomic number elements [4] may be metallized at high pressure. Therefore, study of metallization of solid

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CH₄ under high pressure is of importance from physical, chemical and technological points of view.

Earlier studies have shown that there were four solid phases of methane discovered using optical and x-ray diffraction measurements at room temperature and pressures of 1.6–37 GPa [5–9]. Phase I has an fcc structure above 1.6 GPa with one molecule in the primitive cell [8]. Phase A has a rhombohedral structure at pressures of 5.3–9 GPa with 21 molecules in a unit cell [9] and its structure is similar to the structure of phase I of CF₄ [10]. X-ray diffraction measurements by Umemoto *et al* [11] indicated that phase B has cubic structure below 16.9 GPa. At pressures above 16.9 GPa, phase B transforms to the cubic high-pressure phase (HP phase), and the HP phase persists to 37 GPa. However, there is less detailed knowledge about the phase transition or phase stability for solid CH₄ at multimegabars. In this paper, we used symmetry modes of Raman scattering as a probe to study the high-pressure behavior of solid CH₄.

2. Experiment

We used a diamond anvil cell (DAC) to create high pressure. Diamonds selected carefully for Raman spectroscopy research with very low birefringence were used for x-ray diffraction and Raman measurements. The tips of the diamonds used for this study were 35 μm with a single level. The high-purity CH₄ 99.99% gas was loaded into the tungsten gasket hole of the DAC at room temperature, and then the sample was clamped and further pressurized by closing two diamonds mechanically via a gear box. The initial sample size was 17 μm in diameter and 8.0 μm in thickness for the first experiment and 17 μm in diameter and 8.5 μm in thickness for the second experiment (the thickness of the sample was determined by interference pattern measurements [12, 13]).

To achieve accurate pressure measurements, a submicron layer of platinum (Pt) was deposited onto the side wall of the gasket hole as a pressure marker [14]. A collimated x-ray beam of 15 \times 25 μm was used to study the volume changes of the Pt deposited on the side wall of the gasket hole. Pressure was determined against the Pt isotherm equation of state [15]. The Raman measurements were carried out at room temperature to 208 GPa using a micro-optical system equipped with a microscope and fiber optics connecting to a spectrometer [16]. The experimental data for separate experiments were recorded by a CCD detector.

3. Results and discussion

Solid CH₄ has three internal modes, ν_1 , ν_2 and ν_3 with frequency (σ) at $\sigma_1 = 2914.2 \text{ cm}^{-1}$, $\sigma_2 = 1526 \text{ cm}^{-1}$ and $\sigma_3 = 3022 \text{ cm}^{-1}$ at zero pressure [7]. In this study, attention was focused on mode ν_1 and ν_3 . Figure 1 shows Raman spectra of solid CH₄ at different pressures. The frequencies of ν_1 and ν_3 shift to the high-wavenumber side as pressure increases. The pressure dependence of the Raman frequencies of CH₄ for two experiments is summarized in figure 2. At pressure below 12 GPa, the wavenumber of mode ν_1 and ν_3 as a function of pressure has a small difference on the slope due to the fact that CH₄ undergoes several phase transitions [7]. We found that the frequencies of ν_1 and ν_3 increased linearly with pressure in the pressure range of 34–208 GPa, which may suggest that there is no phase transition in solid CH₄; in other words, solid CH₄ may retain HP phase structure to 208 GPa. Curve fitting yields

$$\sigma_1(\text{cm}^{-1}) = 3154.5(\pm 4.22) + 1.11(\pm 0.03)P \text{ (GPa)} \quad (1)$$

$$\sigma_3(\text{cm}^{-1}) = 3268.7(\pm 6.76) + 1.94(\pm 0.05)P \text{ (GPa)}. \quad (2)$$

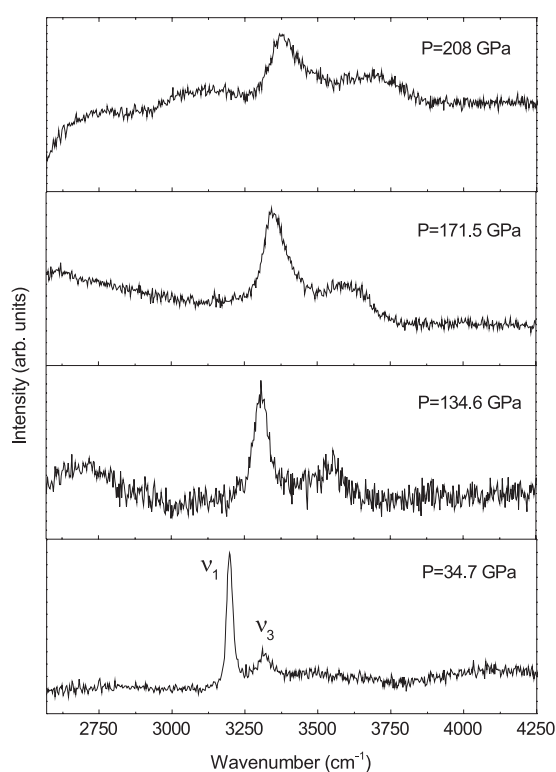


Figure 1. Solid CH₄ Raman spectra at high pressures.

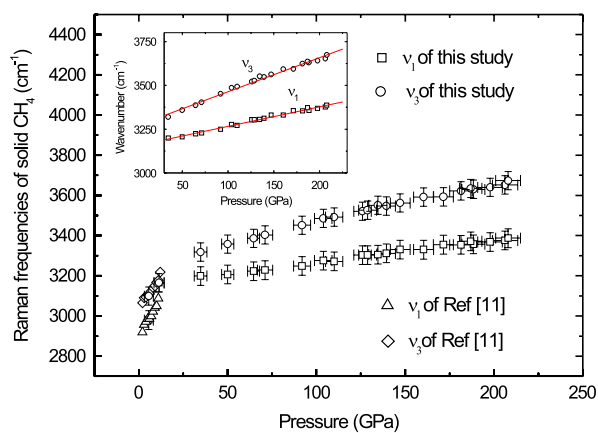


Figure 2. Raman frequencies of solid CH₄ as a function of pressure to 208 GPa. The open squares and circles represent mode ν_1 and mode ν_3 for two separate experiments and the open diamonds and triangles are data points of [7].

(This figure is in colour only in the electronic version)

The $P(V)$ isotherm for the HP phase of CH₄ has been studied by synchrotron x-ray diffraction from 16.9 to 37 GPa [11]. Inasmuch as the Vinet equation gives an excellent fit for the molecular solid H₂ to high pressure [17], it was used to fit the data of [11]. The Vinet

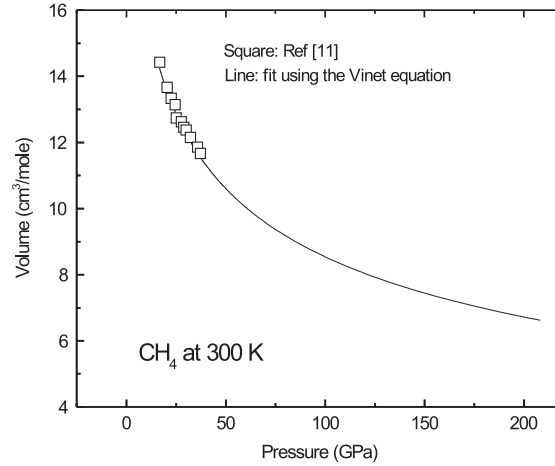


Figure 3. The volume of solid CH₄ as a function of pressure. Solid squares are data points obtained from [11] and the line is our fit using the Vinet equation of state.

equation is given by [18]

$$P = 3K_0 \left(\frac{V}{V_0} \right)^{-\frac{2}{3}} \left[1 - \left(\frac{V}{V_0} \right)^{\frac{1}{3}} \right] \exp \left\{ \frac{3}{2} (K'_0 - 1) \left[1 - \left(\frac{V}{V_0} \right)^{\frac{1}{3}} \right] \right\} \quad (3)$$

where K_0 is the bulk modulus at room pressure, K'_0 is the first derivative of the bulk modulus at zero pressure and V_0 is the volume in the Vinet equation of state at zero pressure. This results in values of $K_0 = 6.4 \pm 0.73$ GPa, $K'_0 = 5.68 \pm 0.36$ and $V_0 = 25.44$ cm³ mol⁻¹. Figure 3 shows the volume of CH₄ as a function of pressure. It should be noted that the volume of CH₄ changes from 11.84 to 6.63 cm³ mol⁻¹ as pressure increases from 34 to 208 GPa.

In earlier studies, the Goldhammer–Herzfeld (GH) equation has been used as a simple criterion for insulator–metal transition of materials such as gases and alkali hydrides. From the Lorentz–Lorenz equation

$$\frac{n^2 - 1}{n^2 + 2} = \frac{R}{V}. \quad (4)$$

Goldhammer and later Herzfeld assumed R did not change with V (or P) and noted that when $n \rightarrow \infty$

$$\frac{R}{V} = 1. \quad (5)$$

Metallization occurs when V decreases to R . Here n is the refractive index, R is the molar refraction and V is the molar volume. According to the GH criterion, metallization for BaTe [19] and xenon [20] occurs at $V = R$. The molar refraction of methane at low pressure is $R = 6.54$ cm³ mol⁻¹ [21]. From the extrapolated equation of state (EOS) the metallization pressure of solid CH₄ is 220 GPa, for which the volume, V , is equal to R .

Recently our reflectivity and absorption measurements to 288 GPa [22] indicated that the molar refraction (R) of solid CH₄ is not constant with pressure. The value of R/V increased linearly as pressure increased. A significant jump in refractive index, absorption coefficient and R/V at 288 GPa suggested that solid CH₄ has changed to a semiconductor at this pressure and room temperature (the R/V value at 288 GPa is very close to the R/V value of silicon).

On the basis of the extrapolated EOS, it is noted that the 11.3% volume change has been observed as pressure increases from 208 to 288 GPa. If the volume at 288 GPa is reduced to

$5.88 \text{ cm}^3 \text{ mol}^{-1}$ by increased pressure and this is followed by a phase transition with a 20.9% volume decrease (as occurs in silicon from the diamond cubic to the β -Sn structure [23, 24]) to $4.65 \text{ cm}^3 \text{ mol}^{-1}$, i.e. to R , a rough estimation of the metallization pressure of solid CH_4 would be about ~ 520 GPa at room temperature.

4. Conclusion

High-pressure Raman spectra of solid methane have been studied to 208 GPa at room temperature. We found that the symmetry modes ν_1 and ν_3 increased linearly as pressure increased from 34 to 208 GPa. Based on x-ray diffraction measurements for the HP phase of solid methane [11], the data points from 16.9 to 37 GPa were fitted using the Vinet equation of state and extrapolated to 208 GPa, which gives $K_0 = 6.4 \pm 0.73$ GPa, $K'_0 = 5.68 \pm 0.36$ and $V_0 = 25.44 \text{ cm}^3 \text{ mol}^{-1}$. Taking a first phase transition into account at 288 GPa [22], the metallization pressure of solid CH_4 at room temperature has been estimated to be about 520 GPa.

Acknowledgments

We wish to thank the National Natural Science Foundation of China through grant no. 50571111 and the National Science Foundation (NSF) through grant no. DMR-0304745 for the support of this research. We also wish to thank the support of the following facilities used in this study: Cornell High Energy Synchrotron Source via grant DMR-0225180 and Cornell Center for Material Research via grant DMR-0079992. This work was also supported by the Ministry of Science and Technology of China (2005CB724400).

References

- [1] Ashcroft N W 2004 *Phys. Rev. Lett.* **92** 187002
- [2] Shimizu K, Ishikawa H, Takao D, Yagi T and Amaya K 2002 *Nature* **419** 597
- [3] Nagamatsu J, Nakagawa N, Muranaka T, Zenitana Y and Akimitsu J 2001 *Nature* **410** 63
- [4] Ruoff A L 2004 private communication
- [5] Bini R and Pratesi G 1997 *Phys. Rev. B* **55** 14800
- [6] Bini R, Ulvi I, Jodi H J and Salvi P R 1995 *J. Chem. Phys.* **103** 1353
- [7] Hebert P, Polian A, Loubeyre P and LeToullec R 1987 *Phys. Rev. B* **36** 9196
- [8] Hazen R M, Mao H K, Finger L W and Bell P M 1980 *Appl. Phys. Lett.* **37** 288
- [9] Nakahata I, Matsui N, Akahama Y and Kawamura H 1999 *Chem. Phys. Lett.* **302** 359
- [10] Fitch A N and Cockoft K 1993 *Kristallografiya* **203** 29
- [11] Umemoto S, Yoshi T, Akahama Y and Kawamura H 2002 *J. Phys.: Condens. Matter* **14** 10675
- [12] van Straaten J and Silvera I F 1988 *Phys. Rev. B* **37** 6478
- [13] van Straaten J, Wijngaarden R J and Silvera I F 1982 *Phys. Rev. Lett.* **48** 97
- [14] Sun L, Ruoff A L and Stupian G 2005 *Appl. Phys. Lett.* **86** 014103
- [15] Wang Y, Ahuja R and Johansson B 2002 *J. Appl. Phys.* **92** 6616
- [16] Zha C S and Bassett W A 2003 *Rev. Sci. Instrum.* **74** 1255
- [17] Loubeyre P, LeToullec R, Hausermann D, Hanfland M, Hemley R J, Mao H K and Finger L W 1996 *Nature* **383** 702
- [18] Vinet P, Ferrante J, Smith J R and Ross J H 1986 *J. Phys. C: Solid State Phys.* **19** 467
- [19] Grzybowski T A and Ruoff A L 1984 *Phys. Rev. Lett.* **53** 489
- [20] Chan K S, Huang T L, Grzybowski T A, Whetten T J and Ruoff A L 1982 *Phys. Rev. B* **26** 7116
- [21] Lide D R 1996 *Handbook of Chemistry and Physics* (Boca Raton, FL: CRC Press)
- [22] Sun L, Ruoff A L, Zha C S and Stupian G 2006 *J. Phys. Chem. Solid* **67** 2603
- [23] Hu J Z, Merkle L D, Menoni C S and Spain I L 1986 *Phys. Rev. B* **34** 4679
- [24] Ducloux S J, Vohra Y K and Ruoff A L 1990 *Phys. Rev. B* **41** 12021