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The Phase Diagram of the Solid Methanes

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A comparative study is presented of the phase diagrams of the solid methanes CH_4, CH_3D, CH_2D_2, CHD_3, and CD_4 obtained experimentally using NMR techniques at pressures up to 9 kbar. Polynomial representations of the I–II, I–III and II–III phase transition lines are given. The experimental conditions under which solid methane transforms to phase IV are discussed and polynomial representations of the I–IV, the IV–I, and the IV–II transition lines are also given.

KEY WORDS: high pressure; isotope effects; methane (solid); nuclear magnetic resonance; phase diagrams.

1. INTRODUCTION

As is well known [1–4], at ambient pressure methane and its deuterated derivatives freeze into an orientationally disordered structure, phase I, at about 90 K. Subsequently, on lowering the temperature, a transformation to a partially ordered phase II occurs in all the methane species. The smaller the amount of deuteration, the lower the transition temperature. Upon further cooling, the deuterated derivatives of methane transform into a structure which is probably a completely orientationally ordered phase III, again with a considerable isotope effect on the transition temperature. At pressure values above a few kilobars, solid methane transforms into a structure called phase IV which, by adjusting the pressure and temperature, may be maintained down to zero pressure. The question remains open whether, at zero pressure, phase IV is stable and phase III an unstable

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configuration; certainly, at elevated pressures, phase III is unstable. Other high-pressure phases have been reported in the literature [5].

We omit a discussion of the wealth of fascinating structural and dynamical properties of solid methane and confine ourselves to a comparative study of the effects of pressure on the position of the various phase transitions. Emphasis is placed on the accurate determination of the transition temperatures and pressures.

2. EXPERIMENTAL METHODS AND RESULTS

Nuclear magnetic resonance (NMR) techniques are very well suited to record a transformation from one configuration of a solid to another. The spin-lattice relaxation time T_1, for instance, is very sensitive to structural and dynamical changes accompanying a phase transition. This is shown in Fig. 1, where the II–III transition of CD_4 at zero pressure is reflected as a discontinuity in T_1 with a small temperature hysteresis.

In order to produce a well-defined pressure, the solid must be subjected to isotropic pressure. For solid methane, the only suitable pressure-transmitting medium is helium, as other pressure fluids would be solid in the temperature and pressure range where the phase transitions in solid methane take place. Even when helium is used, part of the p–T diagram of

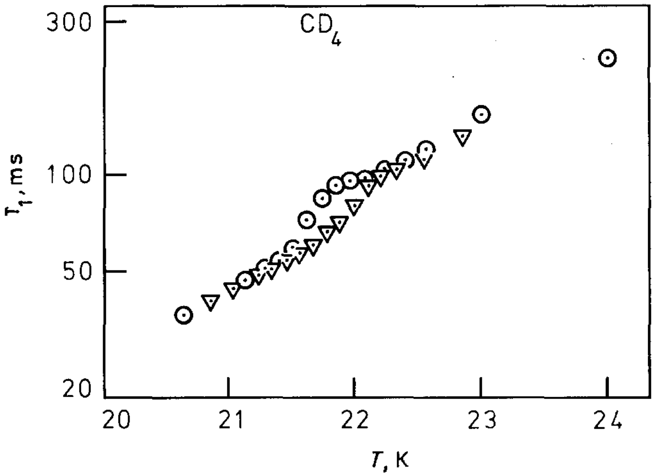

Fig. 1. Behavior of the deuteron relaxation time T_1 at the II–III transition in CD_4 at ambient pressure. (⊙) Decreasing temperature; (▽) increasing temperature.

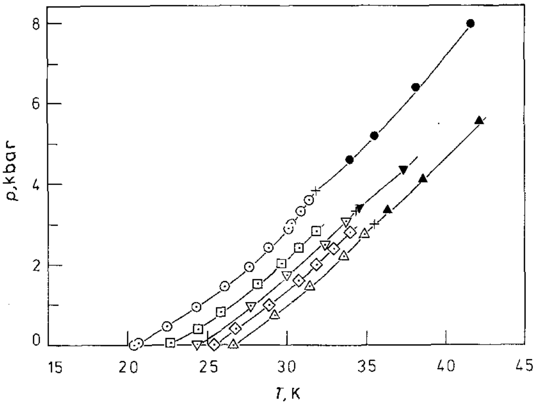

Fig. 2. The I–II and the I–III phase transition lines of the solid methanes up to 8 kbar. (⊙) CH_4; (⊡) CH_3D; (▽) CH_2D_2; (◇) CHD_3; (△) CD_4. The triple points are represented by the crosses. Note that the I–III phase line is metastable above 6 kbar.

solid methane is inaccessible for isotropic pressure, the boundary being the melting line of helium. Below the helium melting line, solid methane can still be subjected to pressure, although the pressure values must then be calculated using the equation of state for solid helium. Of course, the accuracy in pressure will be greatly reduced. For further experimental details, see Refs. 2–4.

The I–II and II–III phase transition lines of the solid methanes up to 5 kbar [2–4, 6] (1 bar = 10^5 Pa) are shown in Figs. 2 and 3. Due to the relatively large zero-point energy of the ordered CH_4 molecules, phase III can be obtained only by applying a pressure of approximately 400 bar, as found by Nijman and Trappeniers [2], who also showed that the minimum of the II–III phase line occurs as a consequence of a sign reversal of

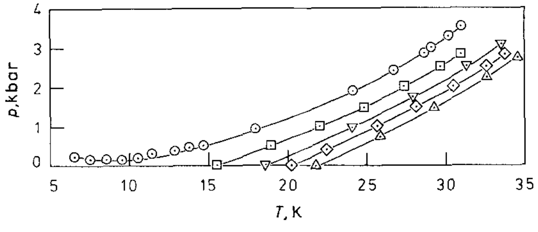

Fig. 3. The II–III phase transition lines of the solid methanes. The symbols used are identical to those in Fig. 2.

the entropy change ΔS, associated with the II–III transition occurring at low temperatures. In the high-temperature limit, the entropy of a free rotor molecule (one-fourth of the molecules in phase II are free rotors) is larger than that of an ordered molecule. At low temperatures, when spin conversion from the $T(I=1, J=1)$ to the $A(I=2, J=0)$ spin species of the free rotor molecules is complete, the fivefold degeneracy of the A level leads to a value of kln5 per molecule for the entropy of the disordered molecules. The ordered molecules in phase III still have kln16 as a result of the 16 closely spaced tunnel levels of the three spin isomers in their librational ground state. Consequently, at low temperatures ΔS at the II–III transformation will be positive, resulting in a negative slope of the II–III phase boundary at lower temperatures.

From an analysis of the isotope effect on the I–II phase transition temperatures, Sprik et al. [6–8] inferred that zero-point motion effects are only partly responsible for the rapid increase in the transition temperature with density. Part of it originates from the strong radial dependence of the effective ordering interaction, with an exponent $n=15$. In a corresponding-state analysis of the isotope effect in quantum crystals Sprik et al. also showed that quantum mechanical effects (zero-point motion) play a major role in suppressing the transition temperatures with a decreasing amount of deuteration of the methanes.

The stability range of the partially ordered phase II of solid CH_4 becomes smaller with increasing pressures, culminating in a triple point at $p=3.90$ kbar and $T=32.1$ K. Above the triple point, only the I–III transition is observed.

When the pressure is increased further, the I–III transformation becomes metastable [3, 4]. With the initial experimental starting conditions of $p=6.0$ kbar and $T=100$ K, i.e., far into phase I, the familiar I–III phase transition is observed upon lowering the temperature to 35 K.

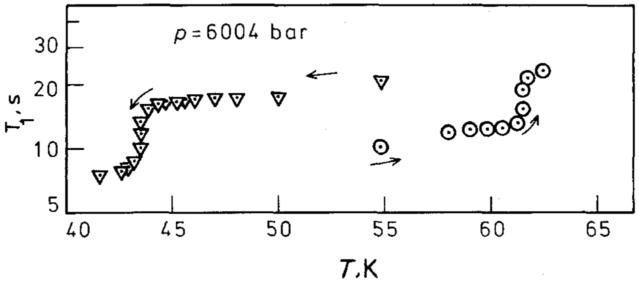

Fig. 4. The hysteresis of the I–IV transition of solid CH_4 at $p=6$ kbar as reflected by the proton T_1.

However, when the solid is maintained in phase I just above the phase transition temperature, T_1 starts to decrease slowly from about 20 s, typical of phase I, to about 5 s in a time span of 3 days. Upon increasing the temperature again, the expected III–I transformation has disappeared. Instead, a first-order discontinuity in T_1 is observed at the much higher temperature of 62 K. When, subsequently, the temperature is reduced again, a second discontinuity is observed 20 K below the previous discontinuity in T_1. This is clear evidence for the occurrence of a phase transition different from the I–III transformation, with a very large hysteresis of about 20 K (Fig. 4). This new phase, called phase IV, is indeed distinct from phase III, as can be inferred from the temperature dependence of T_1 down to 4 K [3, 4]. Phase IV is stable at high pressures (as is reflected in the T_1 versus T curve) upon cycling the temperature between 4 K and the IV–I transition temperature. Once phase IV has been obtained, the IV–I and I–IV transitions occur instantaneously, implying that just above the IV–I transition,

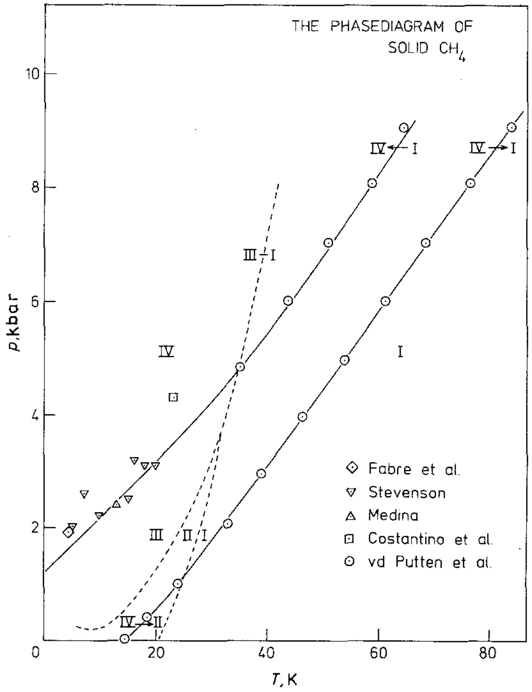

Fig. 5. The phase diagram of solid CH_4. Experimental transition points of the III–IV phase transformation as obtained from a number of different experiments are also shown.

Table I. Polynomial $T = A_0 + A_1 p + A_2 p^2$ Representing the I–II Experimental Transition Points

Substance	A_0 (K)	A_1 (K · kbar^{-1})	A_2 (K · kbar^{-2})
CH_4	20.39	4.56	−0.42
CH_3D	22.80	4.00	−0.27
CH_2D_2	24.39	3.58	−0.17
CHD_3	25.31	3.80	−0.25
CD_4	26.58	3.62	−0.21

Table II. Polynomial $T = A_0 + A_1 p + A_2 p^2$ Representing the II–III Experimental Transition Points

Substance	A_0 (K)	A_1 (K · kbar^{-1})	A_2 (K · kbar^{-2})
CH_4[a]	10.91	8.38	−0.77[a]
CH_3D	15.49	7.14	−0.59
CH_2D_2	18.61	6.03	−0.39
CHD_3	20.24	5.79	−0.34
CD_4	21.79	5.77	−0.42

[a] $p > 1.9$ kbar. The low-pressure transition points of CH_4 ($p < 1.9$ kbar) are given by $p(\text{bar}) = 456 - 15.74T^2 + 2.04T^3 - 0.079T^4 + 1.06 \cdot 10^{-3}T^5$.

Table III. Polynomial $T = A_0 + A_1 p + A_2 p^2$ Representing the I–III Experimental Transition Points

				Triple point	
Substance	A_0 (K)	A_1 (K · kbar^{-1})	A_2 (K · kbar^{-2})	p_{tr} (kbar)	T_{tr} (K)
CH_4	25.10	1.97	0.014	3.90	32.1
CH_3D				3.80	34.1[a]
CH_2D_2	18.83	5.96	−0.39	3.34	34.4
CHD_3				2.94	34.3[a]
CD_4	24.53	4.09	−0.16	3.02	35.5

[a] Extrapolated values (Ref. 6).

Table IV. Polynomial $T = A_0 + A_1 p + A_2 p^2$ Representing the I–IV Experimental Transition Points

Substance	A_0 (K)	A_1 (K · kbar^{-1})	A_2 (K · kbar^{-2})	
CH_4	−8.36	10.00	−0.22	($4.8 < p < 9.1$)
CH_2D_2	−30.05	17.65	−0.72	($5.0 < p < 8.3$)
CD_4	−24.99	16.79	−0.68	($5.5 < p < 7.5$)

phase I retains a memory of phase IV. At a pressure above 6 kbar and on lowering the temperature from far into phase I, the I–III transformation can still be observed up to about 8 kbar. However, phase III becomes increasingly unstable with increasing pressure, i.e., the time constant involved in the transformation from phase III to phase IV becomes smaller to the extent that phase III cannot be obtained above 9 kbar even with a fast cooldown from phase I. The fact that phase IV, and not phase III, is definitely stable at elevated pressures has been shown previously in a diamond-anvil experiment on solid CH_4 [9], where in a pressure range of 20–60 kbar, the volume changes at the I–IV and IV–I transition were used to establish the phase transition points. The hysteresis in the latter experiment was also about 20 K. We note that the diamond-anvil cell experiments involve only the pure substance, which indicates that effects of the pressure fluid on the position of the phase lines are negligible. An interesting phenomenon occurs when, through an adjustment of pressure and temperature, phase IV can be obtained at zero pressure. It appears that below 14.5 K and zero pressure, phase IV is stable for at least several days. This observation raises the question whether the low-temperature phases II and III of solid methane are, in fact, stable.

The various phase lines of solid CH_4 are shown in Fig. 5. Polynomial representations of the phase lines of the solid methanes are given in Tables I–V.

Table V. Polynomial $T = A_0 + A_1 p + A_2 p^2 + A_3 p^3$ Representing the IV–I and IV–II Experimental Transition Points

Substance	A_0 (K)	A_1 (K · kbar^{-1})	A_2 (K · kbar^{-2})	A_3 (K · kbar^{-3})
CH_4	14.76	9.56	−0.48	0.030
CH_2D_2	15.88	11.66	−1.02	0.066
CD_4	16.31	13.80	−1.64	0.117

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