

Research Article

Effect of Molecular Rotational Degrees of Freedom on Mechanical and Thermodynamic Properties of Solid Methane at Temperatures above 50 K

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The paper presents an analysis of extensive data set of mechanical, structural, thermophysical, and spectral properties of solid methane in the temperature interval $0.5 \cdot T_{\text{tr}} - T_{\text{tr}}$ (T_{tr} is the triple point temperature) under equilibrium vapor pressure. It is shown that the anomalies of the studied properties (or lack of reliable data) at temperatures 60–70 K have been observed in the body of the reviewed papers. We proposed that the observed anomalies are due to a transition between classical and quantum regimes of collective rotational degrees of freedom of methane molecules in this temperature interval.

1. Introduction

The development of far cosmos research and discovery of atmospheres at some planets of the Solar System have inspired new large interest to mechanical and thermodynamic properties of solidified gases, in particular, solid methane [1].

Solid methane is the lightest representative among the group of the simplest molecular crystals, formed by CX_4 tetrahedral molecules with 4-3m symmetry [2], where X is hydrogen isotopes or halogen atoms F, Cl, and so forth or their isotopes.

In this paper, we present a detailed analysis of the experimental data of many authors on mechanical, structural, thermophysical, and spectral properties of solid methane in temperature interval $0.5 \cdot T_{\text{tr}} - T_{\text{tr}}$ (T_{tr} is the triple point temperature) under equilibrium vapor pressure. The body of reviewed papers shows the presence of anomalies of above properties at temperatures 60–70 K, or the reliable data are absent. We suppose that these anomalies are caused by a

sudden change of rotational degrees of freedom of CH_4 molecules at temperatures between 60 and 70 K [3].

2. Some Data on Thermodynamic Properties of Solid Methane

Methane is the most examined crystal of CX_4 group. The well-known reviews [4, 5] have presented extensive data on thermodynamic, structural, and mechanical characteristics of solid methane. However, the anomalies of a series of solid methane properties at temperatures higher than $0.5T_{\text{tr}}$ were not mentioned in these reviews.

Under equilibrium vapor pressure, crystalline methane (triple point temperature $T_{\text{tr}} = 90.67$ K [4]) undergoes a λ -type phase transition at $T_{\lambda} = 20.48$ K [3]. In both phases, low-temperature II and high-temperature I, carbon atoms form a FCC lattice (space group Fm3m [4]). It is commonly supposed that in low-temperature phase carbon atoms are ordered in the lattice (expected space group Fm3c or P4-3m

[4]) and make certain librational vibrations relative to the center of inertia of methane molecule and also reorientational hopping from one equilibrium position to another. In phase I, hydrogen atoms entirely loose the ordering and make “hindered spherical rotation” relative to the gravity center of hydrogen atom. Volume jump at the phase transition I-II is about 0.3% [4].

3. Essential Experimental Data: Analysis and Discussion

The problem of the change of methane molecule’s rotational state at temperatures 60–70 K was firstly established by Tomita [3]. In this paper, he studied NMR spectra of solid methane and had revealed that (i) half width of resonance absorption lines $H_{1/2}$ decreases suddenly (see Figure 1) and (ii) time of spin-lattice relaxation changes essentially at temperatures below 60 K (see Figure 2). Accounting of the above-mentioned facts that in a narrow range of temperatures the activation energy of rotation of the methane molecule is increased by about twenty times, Tomita came to the conclusion that after 60 K there is a transition from the hindered rotation of methane to almost free. We can suggest that at temperatures above 60 K the methane molecules turn to a new rotational state, namely, to essentially free (or slightly hindered) rotation such as molecular behavior in liquid phase [6]. In this case, the noncentral intermolecular interaction is almost absent and the contribution of van der Waals central forces becomes dominant in the intermolecular interaction.

Note that this transformation of rotational behavior of methane molecules is displayed not only in the NMR parameters.

Figure 3(a) shows the temperature dependence of low frequency internal friction (LFIF) of solid methane Q^{-1} that has been studied by an inverse torsion pendulum method at frequencies 5–10 Hz and magnitude of deformation $5 \cdot 10^{-5}$. Figure 3(b) presents the temperature dependence of the dynamic shear modulus G derived from the frequency of torsion oscillations f ($f^2 \sim G$) [7]. Procedure of preparing of optically transparent solid CH_4 specimens of high quality with grain size 0.5–2 mm with free surface and the experimental setup for cryocrystals studying by LFIF method have been reported in [7–9].

It is seen from Figure 3(a) that the key feature of the LFIF spectrum $Q^{-1}(T)$ for a whole temperature range is a high peak near 65 K. Its magnitude reaches the value 10^{-1} that is by a factor of about ten times higher than the magnitude of the peak near temperature of the phase I-II transition. Such anomalous rise of Q^{-1} in CH_4 cannot be explained in the frameworks of conventional classic conception. It is necessary to note that such great LFIF peaks have not observed in the previous studies of cryocrystals with central intermolecular forces, for example, in solid argon [8].

Note that the sharp Q^{-1} anomaly is similar to the behavior of LFIF spectra in solid oxygen [9]. This allows us to suggest that at $T \approx 65$ K the phase transition of latent form in solid methane occurs. It is associated with an abrupt change of the rotational state of CH_4 molecules [10]. Later it has been

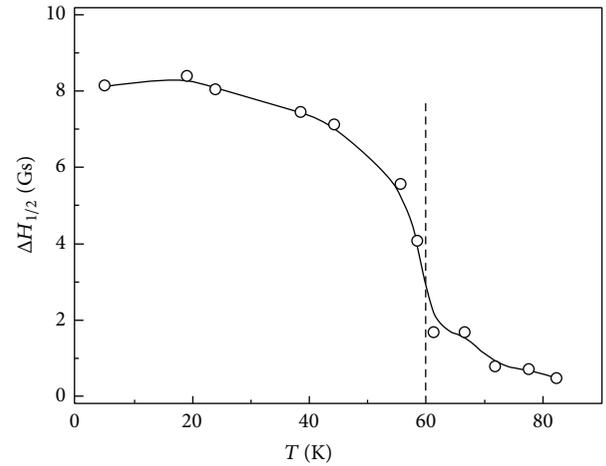


FIGURE 1: Temperature dependence of half width of resonance absorption lines $H_{1/2}$ of the dynamical local field [3].

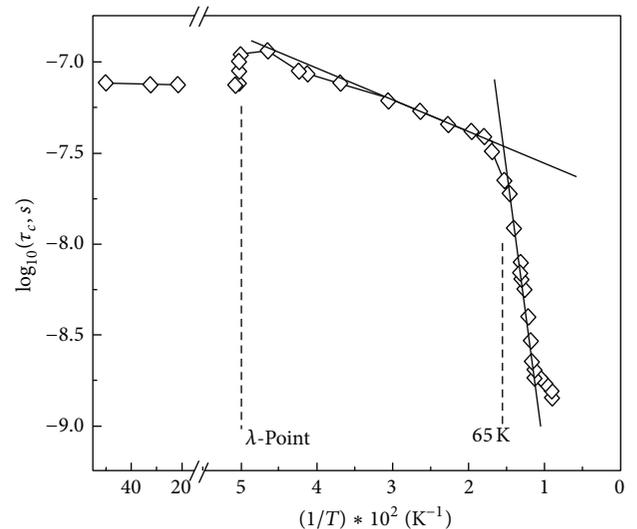


FIGURE 2: The dependence of characteristic time τ_c of spin-lattice relaxation on reciprocal temperature [3].

shown that a set of the observed anomalies can be explained by existence of collective rotational degrees of freedom in solid methane [11].

It is necessary to note that [11] does not provide a report on rotation of separate methane molecules. With the lowering of temperature a collectivization of the rotational degrees of freedom of methane molecules occurs with a new effective moment of inertia of corresponding quasi-particles (topons) at gradual transition of a crystal to the quantum tunnel state of the rotational degrees of freedom of methane molecules occurs with a new effective moment of inertia of corresponding quasi-particles (topons) at gradual transition of a crystal to the quantum tunnel state.

The temperature dependence of $f^2(T)$ also shows a clearly defined minimum near 65 K indicating a significant alteration of intermolecular forces in a narrow temperature

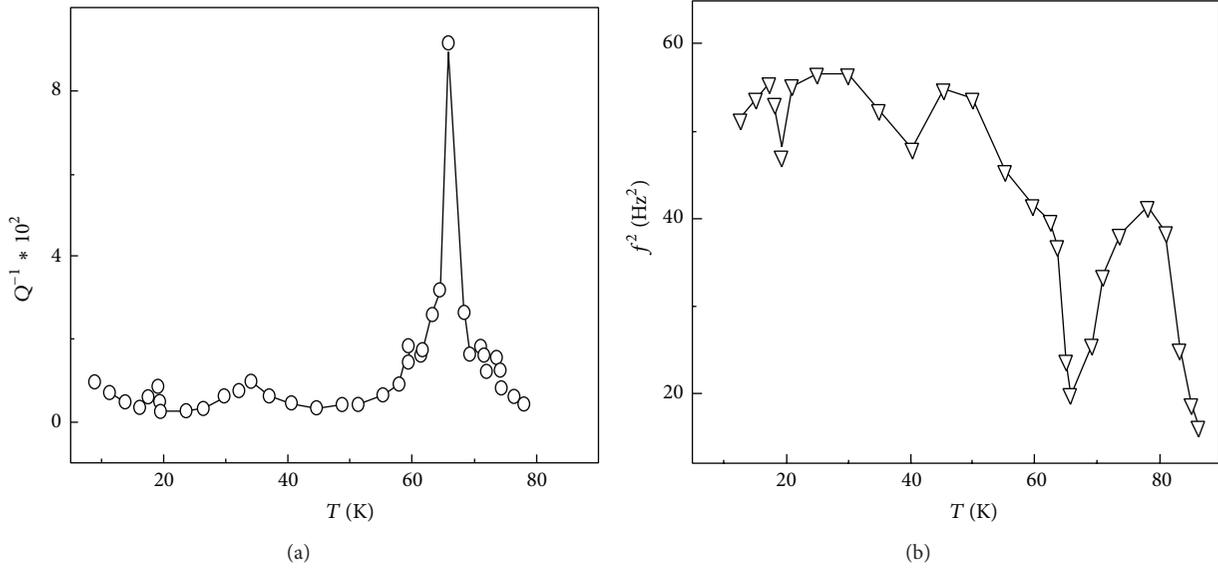


FIGURE 3: Temperature dependence of LFIF Q^{-1} (a) and square of torsion oscillations frequency f^2 (b) of solid methane [7].

interval (3–5 K) (Figure 3(b)). This also can be related with the abovementioned change of rotational movement of CH_4 molecules in temperature interval 60–70 K that affects the mechanical characteristics of solid methane.

Such a conclusion is in agreement with the results of recent work [1] which is devoted to study of adhesion and plasticity of polycrystalline methane in temperature interval 10–90 K. The authors have shown that the adhesion is strong in temperature range 50–90 K where solid methane is soft and sticky. Towards melting temperature, solid methane behaves as very viscous non-Newtonian liquid, but at temperatures below 30 K it loses its “stickiness and plasticity” and behaves like an ordinary glass.

However, despite the mentioned temperature interval 50–90 K of softness and plasticity of solid methane, in the same work [1], after studying of temperature dependence of shear corresponding to a connection breaking point between the solid methane and the special probes, it has been revealed that the shear stress is raised with temperature up to 60 K and then rapidly decreases with temperature approaching to the melting point (see Figure 6 in [1]). This fact directly indicates the alteration of intermolecular forces character in solid methane that is possibly associated with the transition of methane molecules to a new rotational state at temperatures above 60 K.

Analysis of the available experimental data on various properties of solid methane shows that the change of rotational movement of methane molecules is displayed not only in the abovementioned NMR and mechanical characteristics.

Thus, for example, anomalies of elastic properties of solid methane in temperature interval 60–70 K have been reported in [12, 13]. Figure 4 shows that anomalies of the temperature dependence of longitudinal sound velocity $v_l(T)$ have been observed not only near the phase transition but also at temperatures near 60 K. Similar peculiarities have

been observed in [13] for the velocities of both longitudinal v_l and transverse v_s sound (see Figure 5).

It is important to note that although the paper [12] is mentioned in the reviews [4, 5], but nothing more, its results have not been analyzed. As concerns the paper [13], its results have been cited in the reviews both for velocity of longitudinal and transverse sound. The peculiarities of sound velocity [13] are clearly seen in corresponding figures of [4, 5] like as in Figure 5 of this work. Nevertheless, neither authors of [13] nor those of [4, 5] have not considered the anomalous behavior of the temperature dependence of sound velocity near $T = 65$ K.

It should be emphasized that, as distinct from mechanical properties, the anomalies of thermodynamical properties of solid methane in analyzed temperature range are expressed more weakly.

Figure 6 presents the temperature dependencies of molar volume V_m of solid methane reported in [14–16] by several independent research groups. It is clearly seen that $V_m(T)$ [14] shows a peculiarity near 60 K, and jointing of the data [15, 16] yields practically a repetition of $V_m(T)$ from [14]. Anomalies of $V_m(T)$ slightly exceed an experimental error of [14–16]. Even though they are small, they also can be associated with the transition of CH_4 molecules to a new rotational state.

Figure 7 shows the temperature dependencies of the coefficient of volume expansion $\beta(T)$ according to [15, 17–19]. It is seen that the data divergence of various papers exceeds the possible experimental errors. Demating of the results [15, 19] is similar to the peculiarities observed in $V_m(T)$ behavior. Quite possible is that this demating is also related to the above alteration of rotational state of methane molecules. It is interesting to note that since X-ray results [17] do not show any visible feature of $\beta(T)$ however the authors of [17] have observed a certain rise of $\beta(T)$ at temperatures above 70 K in comparison with the estimated dependence for ideal lattice (see Figure 3 in [17]). Besides, it is seen in

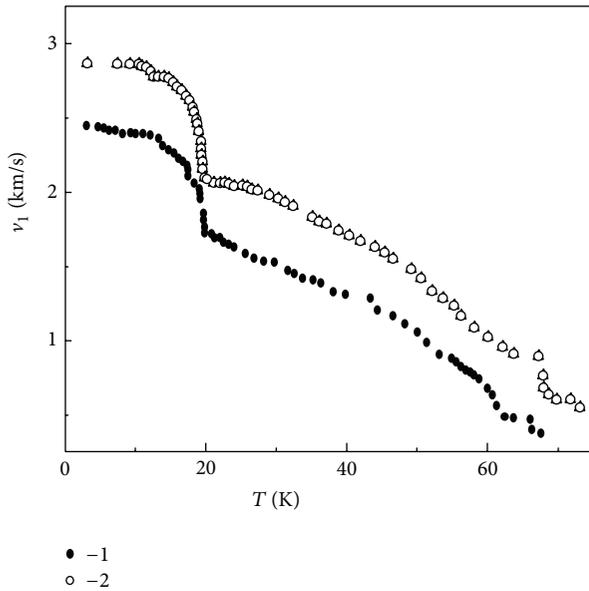


FIGURE 4: Temperature dependence of longitudinal sound velocity v_l [12] for the samples prepared at various growth rates: 1: fast growth and 2: slow growth.

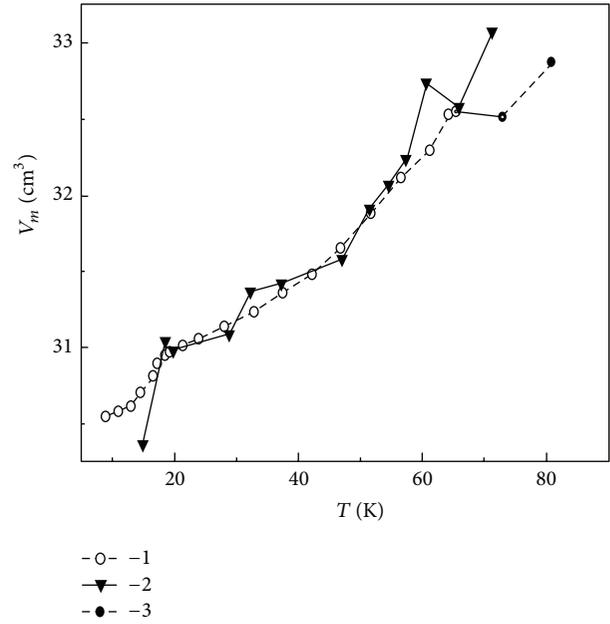


FIGURE 6: Temperature dependencies of molar volume for solid methane according to [14–16]: 1: [15], 2: [14], and 3: [16].

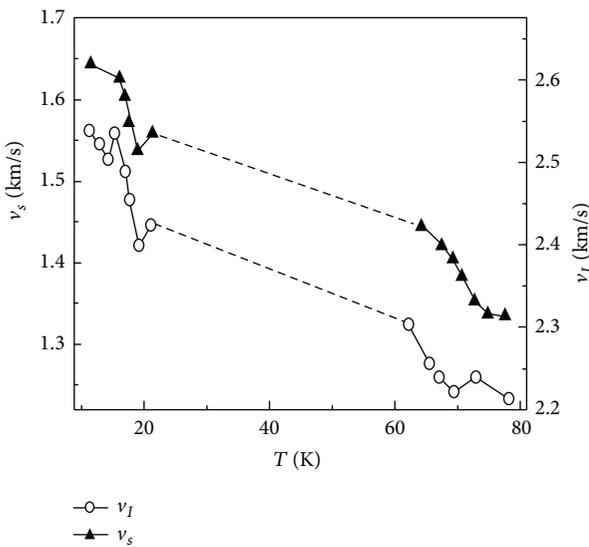


FIGURE 5: Temperature dependence of the velocity of longitudinal v_l and transverse v_s sound of solid methane [13] in the vicinity of the phase transition temperature and in temperature interval 60–80 K.

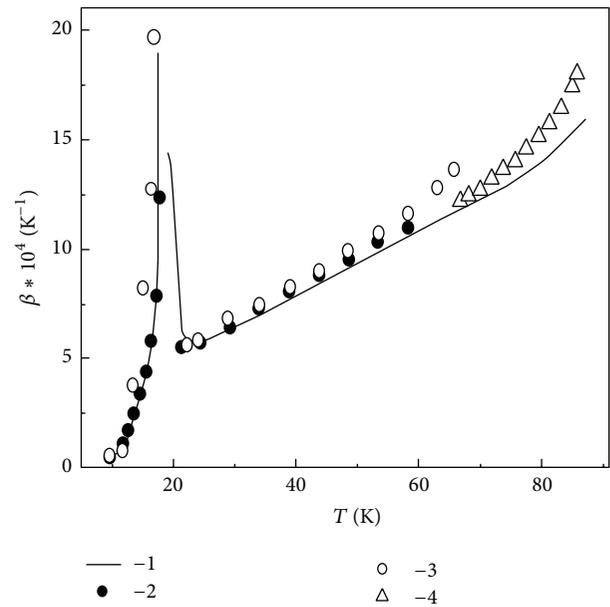


FIGURE 7: Temperature dependencies of volume coefficient of thermal expansion β for solid methane according to the data of several papers: 1-[17]; 2-[18]; 3-[15]; 4-[19].

Figure 7 that, at temperatures above 70 K, $\beta(T)$ obtained from dilatometric measurements [17] rises faster compared to $\beta(T)$ obtained from X-ray data of [19]. Difference between the data reaches 15% at temperature 89 K (see Table 8.10 in [4]). The authors explain it by point defects arising in the sample just as it was observed in solidified inert gases (i.e., Ar and Kr) at premelting temperatures since “solid methane at high temperatures is the closest to crystalline inert gases” [17]. The authors have emphasized that at this temperature range ($T > 70$ K) “a symmetrical distinction between inert

gases atoms and the methane molecules is absent since the last make a practically free rotation in the lattice” [17].

Some more complex situation arises when analyzing the temperature dependence of heat capacity $C_p(T)$. In the analyzed temperature interval ($0.5 \cdot T_{tr} - T_{tr}$), only data of three papers are available [20–22]. Two earlier of them [20, 21] had not reported any noticeable peculiarities in $C_p(T)$ behavior. But the latest paper [22] which reports the temperature

dependencies of heat capacity for both CH_4 and CD_4 has revealed a certain mismatch between these dependencies (see Figure 8).

It has to be noted that, in contrary to CH_4 , CD_4 can exist in three phases under equilibrium vapor pressure [4]. High temperature phase I and middle one II are similar to the phases I and II of solid methane. Low temperature phase III of CD_4 is characterized by more complex ordering of D atoms relatively to centre of mass of carbon atoms accompanied by lowering of symmetry (space group $P-4m2$ or $P42/mbc$ [4]). Therefore, CD_4 molecules in phase I, such as methane ones, make a hindered rotation around a centre of mass of carbon atoms. It is seen from Figure 8 that $C_p(T)$ data cover a whole temperature range of phase I and do not show any features.

In temperature interval 30–90 K the behavior of C_p is less clear. Inset in Figure 8 shows the $C_p(T)$ dependencies for both methane and deuteromethane. It can be seen that the data for CD_4 are continuous over all temperature interval, but the CH_4 data are absent between 61 and 85 K. Besides, this lack is not commented in [22].

Therefore, the data on CH_4 heat capacity are not in contradiction with the above assumption about cooperative behavior of rotational degrees of freedom of methane molecules. The observed anomalies are caused by a transition of the cooperative excitations quasiparticles from quantum (tunnel) to classical (thermoactivation) behavior.

In regard to CD_4 , it should be noted that moment of inertia of a CD_4 molecule is twice as much as for methane molecule. This leads to the change of temperature interval of the transition. Because of lack of a microscopical theory allowing establishing a relation between moment of inertia of a single molecule and effective moments of inertia of collective excitations (topons), this temperature interval cannot be determined theoretically.

4. Conclusions

The presented analysis of available experimental data about the mechanical, structural, thermophysical, and elastic properties of solid methane in temperature range above $0.5 \cdot T_{tr}$ under equilibrium vapor pressure shows that most of considered papers report the anomalies of the studied properties at temperatures 60–70 K or have not the reliable data at this temperature range.

As it follows from [11], a transition of the collective excitations of methane molecular degrees of freedom from quantum behavior to classic one occurs in this temperature interval. Tomita [3] has interpreted such a process as the change of activation energy of rotational state of methane molecules at temperatures 60–70 K.

Just this transition of collective rotational degrees of freedom of methane molecules from quantum behavior to classical one affects the NMR and LFIF spectra as well as the mechanical properties of solid methane. More weakly this effect is displayed in temperature dependencies of thermodynamic parameters of solid methane.

Thus, the change of rotational state of the methane molecules in temperature interval 60–70 K must considerably

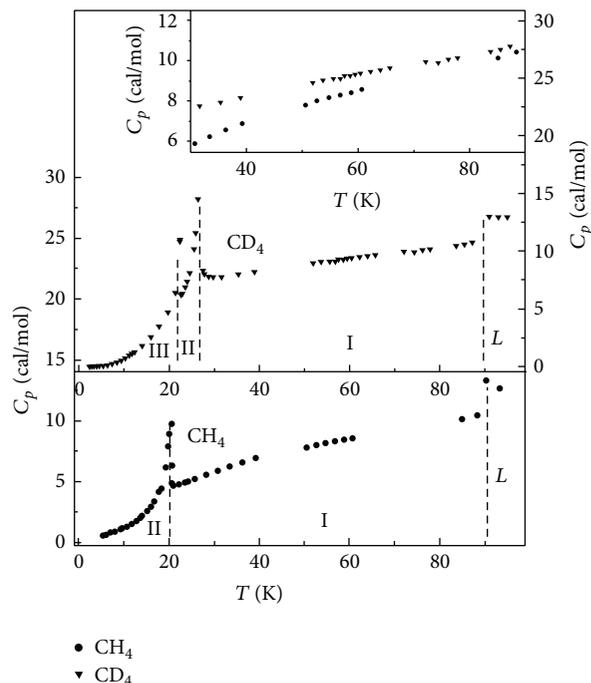


FIGURE 8: Temperature dependencies of heat capacity $C_p(T)$ for CH_4 and CD_4 according to [22].

weaken the intermolecular forces in solid methane. This, in turn, affects its mechanical characteristics. Therefore, results of this paper may be of great importance when analyzing the astrophysical data about the surface of Solar system planets and their satellites.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

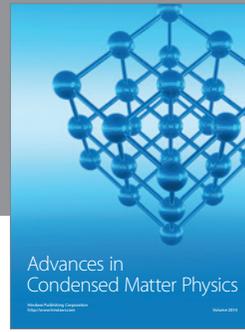
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