The Effect of Pressure on the Negative Thermal Expansion of Solid Methane

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Abstract

The effect of pressure on the thermal expansion of solid CH\textsubscript{4} is calculated for the low temperature region where the contributions from phonons and librons can be neglected and only the rotational tunnelling modes are essential. The effect of pressure is shown to increase the magnitude of the peaks of the negative thermal expansion and shifts the positions of the peaks to the low-temperature region, which goes asymptotically to zero temperature with increasing pressure. The Gruneisen thermodynamical parameter for the rotational tunnelling modes is calculated. It is large, negative, and increases in magnitude with rising pressure.

Keywords: solid methane, negative thermal expansion, Gruneisen thermodynamical parameter
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1. Introduction

At low temperatures the rotational degrees of freedom in solid methane are quantum, which makes solid methane (as well as solid hydrogen), the most interesting simple molecular solids. In addition, the methane molecule has the spin and in the condensed state methane is a mixture of three spin modifications, \( A, T \) and \( E \), the total spins of which is 2, 1 and 0, respectively.

Solid methane has a rich phase diagram with rather unusual orientation structures. The high temperature phase I is orientationally disordered with nearly freely rotating molecules. The I-II transition is driven by the octupole-octupole interaction. The I-II and II-III phase boundaries were first found in the calorimetric measurements by Shubnikov, Trapeznikova and Milyutin \cite{1}. Both CH\textsubscript{4} and CD\textsubscript{4} undergo orientational phase transitions to the partially ordered phase II at 20.4 K and 27.0 K, respectively.

The structure of phase II has been predicted by James and Keenan \cite{2} in 1959 and confirmed for CD\textsubscript{4} using coherent neutron scattering by Press in 1972 \cite{3}. In phase II there are eight sublattices. On two of them the molecular field vanishes; the molecules on these sites do not show orientational order. On the six ordered sublattices the molecules are orientationally ordered.

When temperature decreases, at 22 K CD\textsubscript{4} shows a further transition to a slightly tetragonally distorted phase, whereas CH\textsubscript{4} remains in phase II down to the lowest temperatures. The low-temperature II-III phase boundary was determined by Nijman and Trappeniers \cite{4}. They showed that phase II of CH\textsubscript{4} is reentrant, that is, the phase boundary is curved at low pressure and does not touch the \( P = 0 \) line, so in contrast to solid CD\textsubscript{4} phase III of solid CH\textsubscript{4} exists only under pressure where the II-III phase boundary
goes to the \( P = 0 \) line at 22 K. Below this temperature, only phase III exists. Such difference in the phase diagrams of light and heavy methanes results from the quantum effect of molecular rotation, since the rotational constant \( B_{\text{rot}} = \hbar^2/2I \) of CH\(_4\) is twice as large as that of CD\(_4\) (5.3 and 2.6 cm\(^{-1}\), respectively). Structure of the tetragonal phase was proposed in the x-ray study by Prokhvatilov and Isakina \[5\].

Fabre et al. [6, 7] studied the low-temperature Raman spectra of solid CH\(_4\) up to 9 kbar. The discontinuities observed in the intramolecular and lattice vibrational spectra were indicative the existence of five phases in the pressure range below 9 kbar: phase II (0 - 0.5 kbar), phase III (0.5 - 1.9 kbar), phase IV (1.9 - 4.9 kbar), and phase V (above 4.9 kbar).

The potential barriers arising from intermolecular interactions, hinder free rotation of the methane molecules. Each molecule has several equivalent minima and may tunnel from one position to another resulting in a tunnelling splitting of the rotational levels. Due to this tunnelling, the 16-fold degenerate ground state in phase II is split into a five-fold degenerate level of \( A \) symmetry, a nine-fold \( T \) level, and a two-fold degenerate \( E \) level. The lowest state corresponds to the \( A \) modification, and in the case of noninteracting molecules is characterized by the rotational quantum number \( J = 0 \). The rotational wave function of such a state is spherically symmetric, and the molecule in this state has zero octupole moment. The splittings \( \Delta_{AT} \) and \( \Delta_{TE} \), the energy gaps between the ground state and the \( T \) level and between the \( T \) and \( E \) levels, respectively have been calculated in Refs [8, 9, 10] and measured by the inelastic neutron scattering technique in Refs [11, 12, 13, 14, 15, 16].

The rotational tunnelling states in phases II and III of the compressed solid CH\(_4\) were studied by the inelastic neutron scattering techniques at pressures up to 1.8 kbar [17, 18, 19] and were found that the tunnelling energies strongly depend on pressure. By increasing the pressure from 0.6 to 1.8 kbar the tunnelling lines shift by about a factor of 1.5.

If the barrier height is raised the splittings become smaller. A hydrostatic compression of the solid will increase the barrier height thereby reducing the tunnelling probability and hence decreasing the tunnelling splittings \( \Delta_{AT}, \Delta_{TE} \). The volume change of the crystal with changing temperature (in the temperature range where the the contribution of the usual phonon mechanism is negligible) is determined by the competition between two factors. The contribution to free energy due to populating of the rotational tunnel states of the ordered sublattices on rising temperature favors contracting of the lattice. The height of the potential barriers separating equivalent minima then increases, the magnitude of the tunnelling splitting decreases and the crystal free energy decreases. This effect is counterbalanced by the loss in elastic energy increasing with increased contraction, which stabilizes the crystal volume at each temperature. Thus, rotational tunnelling gives rise to the negative thermal expansion.

Heberlain and Adams [20] found that the thermal expansion coefficient (TEC) of solid methane becomes negative below 8.7 K. Subsequent measurements [21, 22] showed that as the temperature is lowered the absolute value of the TEC being negative continues to grow and at the lowest temperature achieved in the dilatometric measurements (2 K) it is still far from a maximum (Fig 1).

Yamamoto and Kataoka [23] proposed the following qualitative explanation of this phenomenon. The lowest of the splitted 16-fold ground state corresponds to the 5-fold state of the \( A \)-modification, and in the case of noninteracting molecules it is characterized by a rotational quantum number \( J = 0 \). The rotational wave function of such a state is spherically symmetric, and a molecule in this state has zero octupole moment. In the crystal the ground state is a superposition of states with different values of \( J \). However, the \( A \)-modification molecule has a more spherically symmetrical spatial distribution and, consequently, a lower value of the effective octupole moment than \( T \)- and \( E \)-modification
molecules. As the temperature is reduced, the effective intermolecular octupole interaction decreases and, as a result, the crystal volume increases. Conversion is essential for this mechanism to work, producing an increase in the population of the $A$-modification ground state with decreasing temperature. Aleksandrovskii et al. [21, 22] demonstrated the determining role of conversion in this mechanism.

Quantitative theory of the negative thermal expansion of solid methane at zero pressure based on the quantum rotational tunnelling was proposed in Ref. [24]. The effect of pressure on the low-temperature thermal expansion is considered in the present paper.

2. Negative thermal expansion of compressed solid methane

At sufficiently low temperatures when the phonon and libron contributions can be neglected, crystal free energy can be written in the form

$$\mathcal{F} = \mathcal{F}_1(V,T) + \frac{(V-V_0)^2}{2\chi V_0}.$$  \hspace{1cm} (1)

Here $\mathcal{F}_1$ is free energy associated with the tunnelling states of the ordered sublattices:

$$\mathcal{F}_1 = -Nk_B T \ln[5 + 9 \exp(-\Delta_{AT}/T) + 2 \exp(-\Delta_{AE}/T)].$$  \hspace{1cm} (2)

$N$ is the number of sites in the ordered sublattice ($N = (3/4)N_0$), where $N_0$ is the number of molecules. The last term in Eq. (1) is the lattice elastic energy, where $V(T)$ is the volume, $T$ is temperature, $V_0$ is the crystal volume at $T = 0$, and $\chi$ is the isothermal compressibility.

We will not take the existence of the $E$ modification into account in the further calculation. First, it has a lower concentration and second, the contribution of this modifications comes in the temperature region in which the phonon contribution already appears.

So we will start from the free energy

$$\mathcal{F} = -Nk_B T \ln(5 + 9e^{-\Delta/T}) + \frac{(V-V_0)^2}{2\chi V_0},$$  \hspace{1cm} (3)

where $\Delta = \Delta_{AT}$ is the gap between the five-fold degenerate ground state of the $A$ modification and nine-fold levels of the $T$ modification.
The contribution of the tunnelling states into pressure is given by the equation

\[ P = -\left( \frac{\partial F}{\partial V} \right)_T. \tag{4} \]

The volume dependence of \( F \) is connected with the dependence of the energy of the tunnelling states on the internuclear distance. The equilibrium volume of the crystal at temperature \( T \) is determined by the condition for a minimum in free energy (considering the situation at zero pressure) \( \partial F / \partial \Delta V = 0 \), \( \Delta V = V(T) - V_0 \). Since the elastic energy is positive for any value of \( \Delta V \), the sign of the thermal expansion is determined by the sign of the derivative \( \partial F_1 / \partial \Delta V \). It is easy to see that \( \partial F / \partial \Delta V > 0 \) and the thermal expansion is negative. Really, a reduction in crystal volume leads to an increase in the barrier separating equivalent minima, i.e. to a reduction in the tunnelling probability and in tunnelling splitting and, as a result of this, to a reduction in the magnitude of \( F_1 \). The loss in \( F_1 \) is compensated by a gain in elastic energy, which then determines the equilibrium volume \( V(T) \) at each temperatures. The considered mechanism leads to a negative thermal expansion over the whole temperature range of existence of phase II methane. As the temperature is raised, the contribution of the usual thermal expansion mechanism (phonon and libron) starts to grow, and eventually the total thermal expansion of the crystal becomes positive.

From Eq. (5) for the pressure we have the following equation:

\[ P = -9N \frac{e^{-\Delta/k_B T}}{5 + 9e^{-\Delta/k_B T}} \frac{\partial \Delta}{\partial V} \frac{V - V_0}{\chi V_0}. \tag{5} \]

The coefficient of thermal expansion

\[ \beta_P = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P. \tag{6} \]

Let us turn from the variables \( V, T \) to the variables \( P, V \) using the Jacobian of the transformation \( D(P, V)/D(T, V) \). As a result we have

\[ \beta_P = -\left( \frac{\partial P}{\partial T} \right)_V \frac{1}{V(\partial P/\partial V)_T}. \tag{7} \]

From Eq. (5) we have the following relations for the derivatives \( \left( \partial P / \partial T \right)_V \) and \( \left( \partial P / \partial V \right)_T \):

\[ \left( \frac{\partial P}{\partial T} \right)_T = -45N \left( \frac{1}{T} \right) \frac{\exp(-\Delta/k_B T)}{5 + 9\exp(-\Delta/k_B T)^2} \frac{\partial \Delta}{\partial V}. \tag{8} \]

\[ \left( \frac{\partial P}{\partial V} \right)_T = -\frac{1}{\chi V_0} \left\{ 1 - 45N \chi V_0 \frac{(\Delta/k_B T)e^{-\Delta/k_B T}}{(5 + 9e^{-\Delta/k_B T})^2} \left( \frac{\partial \Delta}{\partial V} \right)^2 + 9N \chi V_0 \frac{e^{-\Delta/k_B T}}{5 + 9e^{-\Delta/k_B T}} \frac{\partial^2 \Delta}{\partial V^2} \right\}^{-1}. \tag{9} \]

Finally for the coefficient of thermal expansion we have the following relation:

\[ \beta_P = -45Nk_B \chi \left( \frac{V_0}{V} \right) \left( \frac{\Delta/k_B T^2 e^{-\Delta/k_B T}}{5 + 9e^{-\Delta/k_B T}} \right) \frac{\partial \Delta}{\partial V} \times \]

\[ \left\{ 1 - 45N \chi V_0 \frac{(\Delta/k_B T)e^{-\Delta/k_B T}}{(5 + 9e^{-\Delta/k_B T})^2} \left( \frac{\partial \Delta}{\partial V} \right)^2 + 9N \chi V_0 \frac{e^{-\Delta/k_B T}}{5 + 9e^{-\Delta/k_B T}} \frac{\partial^2 \Delta}{\partial V^2} \right\}^{-1}. \tag{10} \]
Equation (10) should be supplemented by equations for $\Delta$ and $\partial \Delta / \partial V$. We shall use for the further calculations the dependence of the energy of the tunnelling state $\Delta$ at zero pressure on rotational barrier height $U$, obtained by Huller and Raich [9]:

$$\Delta = \omega_0 e^{-\gamma U},$$

were $U$ is the barrier height in units of the rotational constant. Taking into account that repulsive forces make the largest contribution to the the derivative $\partial \Delta / \partial V$ and assuming that there is a power law relation $U \sim r^{-n}$ and taking $n = 15$ [4] we finally have

$$(\partial \Delta / \partial V)_{P,T=0} = 5(\Delta/V_0)(\gamma U_0); \quad (\partial^2 \Delta / \partial V^2)_{P,T=0} = 25(\Delta/V_0^2)(\gamma U_0)^2.$$ (12)

where $U_0$ is the reduced value of the barrier at zero pressure and temperature. The effect of pressure on the thermal expansion of solid methane can be seen from Fig. 2.

The sensitivity of the respective frequency spectrum to the lattice expansion is described by the Gruneisen parameter $G$

$$G = \beta_P V/C_V \chi,$$ (13)

where $C_V$ describes the contribution of the respective modes to the heat capacity $C_V = -T(\partial^2 F_1/\partial T^2)$. For the rotational tunnelling modes from Eq (2) we have

$$C_V^\text{rot} = 45 N k_B (\Delta/k_B T)^2 e^{-\Delta/k_B T} / [5 + 9 e^{-\Delta/k_B T}]^2.$$ (14)

$$G(P) = \frac{V_0 \Delta}{\Delta} \left\{ 1 - 45 \frac{N \chi V_0 (\Delta/k_B T) e^{-\Delta/k_B T}}{5 + 9 e^{-\Delta/k_B T}} \left( \frac{\partial \Delta}{\partial V} \right)^2 + 9 N \chi V_0 e^{-\Delta/k_B T} \frac{\partial^2 \Delta}{\partial V^2} \right\}^{-1}. $$ (15)
At zero pressure

\[ G(P = 0) = -\frac{V_0}{\Delta} \left( \frac{\partial \Delta}{\partial V} \right)_{P=0} = -5\gamma U_0 = -17.2. \] (16)

The pressure dependence of the thermodynamical Gruneisen parameter \( G(P) \) is shown in Fig. 3.

3. Conclusions

The effect of pressure on the thermal expansion of solid \( \text{CH}_4 \) is calculated for the low temperature region where only the rotational tunnelling modes are essential. It is shown that the effect of pressure is quite unusual: the solid \( \text{CH}_4 \) becomes increasingly quantum with rising pressure.

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