Negative Thermal Expansion in Solid Deuteromethane

Yu.A. Freiman†, V.V. Vengerovsky†, and Alexander F. Goncharov⋆

† B.Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine, 47 Nauky Avenue, Kharkiv 61103, Ukraine
⋆Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road NW, Washington D.C. 20015, USA

September 2, 2020

Abstract

The thermal expansion at constant pressure of solid CD₄ III is calculated for the low temperature region where only the rotational tunneling modes are essential and the effect of phonons and librons can be neglected. It is found that in mK region there is a giant peak of the negative thermal expansion. The height of this peak is comparable or even exceeds the thermal expansion of solid N₂, CO, O₂ or CH₄ in their triple points. It is shown that like in the case of light methane, the effect of pressure is quite unusual: as evidenced from the pressure dependence of the thermodynamic Grüneisen parameter (which is negative and large in the absolute value), solid CD₄ becomes increasingly quantum with rising pressure.

Keywords: solid deuteromethane, negative thermal expansion, Grüneisen thermodynamical parameter
PACS 65.40.De

1 Introduction

Heberlain and Adams [1] found that the thermal expansion coefficient (TEC) at constant pressure, βₚ, of solid methane CH₄, becomes negative below 8.7 K. It should be noted that Manzhelii et al. [2] also observed this effect but ascribed it to problems with thermometry. Subsequent measurements [3, 4] showed that as the temperature is lowered the absolute value of |βₚ| continues to grow and at the lowest temperature achieved in the dilatometric measurements (2 K) it is still far from a maximum. Negative thermal expansion in solid methane occurs in the temperature and pressure ranges, where the contribution of phonons and librons to thermodynamics can be neglected compared to that of rotational tunneling states. Due to this tunneling between different orientations the librational ground state is splitted. In the case of CH₄ this tunneling splittings is about 1 K. The existence of these splittings has been confirmed in the NMR experiment by Glattli et al. [5] and by Press and Kolmar [6] in a neutron scattering experiment. Transitions between different states simultaneously include changes in spin and orientation states.

It is easy to see why the rotational tunneling gives rise to the negative thermal expansion. Indeed, the volume change of the crystal with changing temperature (in the temperature range where the contribution of phonons is negligible) is determined by the competition between two factors. The contribution to the free energy due to populating of the rotational tunnel states of the ordered sublattices on rising temperature favors a contracting of the lattice. The height of the potential barriers separating the equivalent

minima then increases, the magnitude of the tunneling 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, this mechanism of the negative thermal expansion is purely quantum.

The theoretical maximum of $|\beta_P|$ at zero pressure which lays at about $0.66 \times 10^{-3} \text{ K}^{-1}$ [7]. The effect of the hydrostatic pressure on the thermal expansion of solid CH$_4$ was calculated in Ref. [8]. It was shown that the magnitude of the peaks of the negative thermal expansion increases with pressure while the peaks shift to the low-temperature region. The effect of pressure can be seen from the following figures: at 1.9 kbar the position of the peak lays at 0.169 K while the height of the peak is $1.77 \times 10^{-3} \text{ K}^{-1}$. It should be noted that it is quite unusual that the quantum effects increase with pressure.

Both CH$_4$ and CD$_4$ have three long-lived spin species, $A$, $T$, and $E$ which transform under the group $T$ as one $A$ representation, three $T$ representations, and one two-dimensional $E$ representation. The experimental observations of the tunneling states in phase II of CH$_4$ (73 and 143 $\mu$eV) [6] have been used to predict the effect on tunneling of an isotopic shift of CH$_4$ to CD$_4$. A conclusion reached was that the tunnel splittings in CD$_4$ would be reduced by about a factor of 50 from those in CH$_4$. Numerous studies are devoted to the investigations of the effects which have place when instead of solid light methane CH$_4$ heavy solid methane CD$_4$ was considered [9].

When nuclear spin and the requirements of the permutation symmetry are taken into account, it is found that only certain values of the total nuclear spin $I$ are associated with each spin species. For CD$_4$, the resulting degeneracies of the tunneling states (and associated $I$ values) of the three spin species are as follows: $A$, 15 ($I = 0, 2, 4$); $T$, 54 ($I = 1, 2, 3$); $E$, 12 ($I = 0, 2$).

The $P - T$ phase diagram of solid deuteromethane CD$_4$ was studied by van der Putten et al. [10] by using the nuclear magnetic resonance at pressures up to 8 kbar and temperatures 10 - 70 K. The phase diagrams of CH$_4$ and CD$_4$ are qualitatively similar [11], except that the phase III of CD$_4$ is stable down to zero pressure while phase III in CH$_4$ exists only under pressure [12]. When temperature decreases, at 22.15 K CD$_4$ shows a further transition to a slightly tetragonally distorted phase [17], whereas CH$_4$ remains in phase II down to the lowest temperatures. Such difference in the phase diagrams of light and heavy methanes results from the quantum effect of the 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). The structure of the tetragonal phase in CD$_4$ was proposed in the x-ray study by Prokhvatilov and Isakina [13]. The dilatometry studies of the lattice parameters, molar volume, and thermal expansion of solid CD$_4$ down to 2 K were performed by Manzhelii group [2, 14]. The x-ray low-temperature data down to 4.4 K were obtained by Baer et al. [15]. The low-temperature measurements of the heat capacity of solid CD$_4$ were carried out by Colwell, Gill, and Morrison, (0.28 - 4.0 K) [16, 17], Colwell [18], White and Morrison (0.15 - 4.0 K) [19], and White [20].

## 2 Negative thermal expansion

In the two-site approximation free energy associated with the rotational tunneling modes can be written as a sum of the rotational free energy and the elastic energy:

$$F(V, T) = -\frac{1}{2} Nk_B T \sum_{\varepsilon \in \{2, m\}} \ln Z_\varepsilon + \frac{(V - V_0)^2}{2\chi V_0},$$  \hspace{1cm} (1)
where $V_0$ is the volume of the system at zero temperature and pressure, $\chi$ is the isothermal compressibility. The summation in Eq. (1) is taken over the sites belonging to symmetries 2 and $m$. The statistical sum $Z_\varepsilon$ can be obtained by the summation over the spectrum of the tunneling rotational modes:

$$Z_\varepsilon = \sum_{i=0}^{4} \alpha_i \exp\left(\frac{-c_i^{(e)} \Delta(V)}{k_B T}\right),$$  \hspace{1cm} (2)

where $\alpha_i$ is the degeneracy of the respective rotational state, $\Delta(V)$ is a difference of the arithmetic mean of the $T$ state energies and the $A$ state energy, and the constants $\{c_i^{(e)}\}_{i=0}^{4}$ can be obtained from the following linear equations:

$$\Delta(V) = 1/3(E_{T_1} + E_{T_2} + E_{T_3}) - E_A,$$

$$E_A(\varepsilon) - E_A = c_0^{(e)} \Delta(V),$$

$$E_A(\varepsilon) - E_A = c_1^{(e)} \Delta(V),$$

$$E_A(\varepsilon) - E_A = c_2^{(e)} \Delta(V),$$

$$E_A(\varepsilon) - E_A = c_3^{(e)} \Delta(V).$$

The contribution of the tunneling states into pressure is given by the equation

$$P = -\left(\frac{\partial F}{\partial V}\right)_T,$$  \hspace{1cm} (3)

From Eq. (3) we have the following equation:

$$P = -\frac{N}{2} \frac{\partial \Delta}{\partial V} \sum_{\varepsilon \in \{2,m\}} \frac{Y_\varepsilon}{Z_\varepsilon} \frac{V - V_0}{\chi V_0},$$  \hspace{1cm} (4)

where

$$Y_\varepsilon = \sum_{i=0}^{4} \alpha_i c_i^{(e)} \exp\left(\frac{-c_i^{(e)} \Delta(V)}{k_B T}\right).$$  \hspace{1cm} (5)

The coefficient of thermal expansion at constant pressure

$$\beta_P = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P.$$  \hspace{1cm} (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

$$\beta_P = -\left(\frac{\partial P}{\partial T}\right)_V \frac{1}{V(\partial P/\partial V)_T}.$$  \hspace{1cm} (7)

From Eq. (7) we have the following relations for the derivatives $\left(\partial P/\partial T\right)_V$ and $\left(\partial P/\partial V\right)_T$:

$$\frac{\partial P}{\partial T} = -\frac{N \Delta(\partial \Delta/\partial V)}{2k_B T^2} \sum_{\varepsilon \in \{2,m\}} \left(\frac{X_\varepsilon}{Z_\varepsilon} - \frac{Y_\varepsilon^2}{Z_\varepsilon^2}\right),$$  \hspace{1cm} (8)

$$\frac{\partial P}{\partial V} = -\frac{1}{\chi V_0} - \frac{N}{2} \sum_{\varepsilon \in \{2,m\}} \left(\frac{Y_\varepsilon}{Z_\varepsilon} \frac{\partial^2 \Delta}{\partial V^2} - \frac{1}{k_B T} \left(\frac{X_\varepsilon}{Z_\varepsilon} - \frac{Y_\varepsilon^2}{Z_\varepsilon^2}\right) \left(\frac{\partial \Delta}{\partial V}\right)^2\right)$$

$$X_\varepsilon = \sum_{i=0}^{4} \alpha_i \left(c_i^{(e)}\right)^2 \exp\left(\frac{-c_i^{(e)} \Delta(V)}{k_B T}\right).$$  \hspace{1cm} (10)

Finally, for the coefficient of thermal expansion we have the following equation:

$$\beta_P = -\frac{N \chi V_0 \Delta(\partial \Delta/\partial V)}{2k_B T^2 V} \sum_{\varepsilon \in \{2,m\}} \left(\frac{X_\varepsilon}{Z_\varepsilon} - \frac{Y_\varepsilon^2}{Z_\varepsilon^2}\right) \times $$
\[
\left\{ 1 + \frac{N\chi V_0}{2} \sum_{\varepsilon \in \{2,m\}} \left( \frac{Y_\varepsilon}{Z_\varepsilon} \frac{\partial^2 \Delta}{\partial V^2} - \frac{1}{k_B T} \left( \frac{X_\varepsilon}{Z_\varepsilon} - \frac{Y_\varepsilon^2}{Z_\varepsilon^2} \right) \left( \frac{\partial \Delta}{\partial V} \right)^2 \right) \right\}^{-1}. \tag{11}
\]

Equation (11) 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 tunneling state \(\Delta\) at zero pressure on the rotational barrier height \(U\), obtained by H"uller and Raich \[21\]. Taking into account that the repulsive forces make the largest contribution to the derivative \(\partial \Delta/\partial V\) and assuming that there is a power law relation \(U \sim r^{-n}\) and taking \(n = 15\) \[33\] we finally have:

\[
\Delta(V) = \omega_0 e^{-\gamma U_0 (V/V_0)^{-5}}, \tag{12}
\]

where \(\omega_0 = \Delta(V_0)e^{\gamma U_0}\). Here \(U_0\) is the reduced value of the barrier at zero pressure and temperature.

From Eq. (12) we have the following equations:

\[
(\partial \Delta/\partial V)_{P,T} = 5(\Delta/V_0)(\gamma U_0) \left( \frac{V_0}{V} \right)^6,
\]

\[
(\partial^2 \Delta/\partial V^2)_{P,T} = 25(\Delta/V_0^2)(\gamma U_0)^2 \left( \frac{V_0}{V} \right)^{12} - 30(\Delta/V_0^2)(\gamma U_0) \left( \frac{V_0}{V} \right)^7. \tag{13}
\]

The effect of pressure on the thermal expansion of solid deuteromethane can be seen from Fig. 1.

The sensitivity of the respective frequency spectrum to the lattice expansion is described by the Grüneisen parameter \(G\)

\[
G = \beta_P V/C_V \chi, \tag{14}
\]

where \(C_V\) describes the contribution of the respective modes to the heat capacity \(C_V = -T(\partial^2/\partial T^2)\). For the rotational tunneling modes from Eq. (1) we have

\[
C_V^{\text{rot}} = \frac{N\Delta^2}{2k_B T^2} \sum_{\varepsilon \in \{2,m\}} \left( \frac{X_\varepsilon}{Z_\varepsilon} - \frac{Y_\varepsilon^2}{Z_\varepsilon^2} \right). \tag{15}
\]

Finally, we have

\[
G(P) = -\frac{V_0}{\Delta} \frac{\partial \Delta}{\partial V} \left\{ 1 + \frac{N\chi V_0}{2} \sum_{\varepsilon \in \{2,m\}} \left( \frac{Y_\varepsilon}{Z_\varepsilon} \frac{\partial^2 \Delta}{\partial V^2} - \frac{1}{k_B T} \left( \frac{X_\varepsilon}{Z_\varepsilon} - \frac{Y_\varepsilon^2}{Z_\varepsilon^2} \right) \left( \frac{\partial \Delta}{\partial V} \right)^2 \right) \right\}^{-1}. \tag{16}
\]

Taking into account Eq. (14), we have

\[
V(T = 0, P) = V_0 (1 - P \chi). \tag{17}
\]

At zero temperature

\[
G(T = 0, P) = -\frac{V_0}{\Delta} \left( \frac{\partial \Delta}{\partial V} \right)_{P=0} = -5\gamma U_0 (1 - P \chi)^{-6}. \tag{18}
\]

\[
G(T = 0, P = 0) = -34.4. \tag{19}
\]

The pressure dependence of the thermodynamical Grüneisen parameter \(G(P)\) is shown in Fig. 2.
Figure 1: The effect of pressure on the thermal expansion of solid deuteromethane. The volume expansion coefficient as a function of temperature: red curve - zero pressure; blue curve - 840 bar.

Figure 2: Thermodynamical Grüneisen parameter of solid methane as a function of pressure.
Figure 3: The minimal volume expansion coefficient as a function of pressure.

Figure 4: The temperature of the minimal volume expansion coefficient as a function of pressure.
3 Numerical results

The rotational tunneling in phase III of CD₄ has been studied by the incoherent neutron scattering in numerous papers [22, 23, 24, 25, 26, 27, 28, 29, 30, 31]. A rather complicated structure of the inelastic neutron scattering spectrum in CD₄ compared to that in CH₄ can only be explained assuming that a superposition of the several single molecule spectra takes place. Prager, Press, and Heidemann [23] proposed a number of the alternative models of the tunneling splittings present in CD₄ III, based on the incoherent neutron scattering data. With the use of the notation of H"uller [32], a given orientational potential is characterized by four overlap matrix elements \( h_1, h_2, h_3, h_4 \) for 120° rotations about the four threefold axes of the molecule, and by three overlap matrix elements \( H_x, H_y, H_z \), for 180° rotations about the three twofold axes of the molecule. In all of these models, the 180° overlap matrix elements are considered negligible compared to the 120° overlap matrix elements. Under this assumption, the energy of the \( E \) states is \(-4h = -(h_1 + h_2 + h_3 + h_4)\), the energy of the \( A \) states is \( 8h \), and the mean energy of the \( T \) states is zero. All the overlap matrix elements are negative, so the \( A \) states are lowest in energy.

In our numerical calculations, we used the two-site model developed by Prager et al. [23] for symmetries 2 and \( m \). For the strength parameters \( h_i \) we used the values obtained from their fit to the inelastic scattering data (see Table II [31]). The following values of the parameters were used in the calculations: \( \chi = 3.4 \cdot 10^{-11} \text{cm}^2/\text{dyn}, \gamma U_0 = 6.88 \), twice as large as in light methane [7]. The minimal value of the thermal expansion of solid deuteromethane as a function of pressure can be seen in Fig. 3. The temperature of the minimum of the thermal expansion of solid deuteromethane as a function of pressure can be seen in Fig. 4.

Concerning the comparison with experiment, the situation is as follows. In the paper [7] the author compared the proposed theory with the available at that time experimental data for light methane. Already at that moment, the experiment has been falling behind the theory. Moreover, this is true today. With regard to deuteromethane, any experimental data on the thermal expansion in the range below 2 K are absent. Meanwhile, the giant peak of the negative thermal expansion predicted in our article and the pressure effects are quite accessible to modern low-temperature experiment.

4 Conclusions

The thermal expansion at constant pressure of solid deuteromethane in the low-temperature phase CD₄ III is calculated for the low-temperature region where the contributions from phonons and librions can be neglected and the whole effect of the thermal expansion is due to the rotational tunneling modes. It is found that in the mK region there is a giant peak of the negative thermal expansion. The height of this peak is so large that it is comparable or even exceeds the thermal expansion of the simple molecular solids N₂, CO, O₂, or CH₄ in their triple points [34, 35]. The effect of pressure is calculated and it is shown that like solid CH₄ solid CD₄ becomes increasingly quantum with rising pressure. Such unusual behavior is due to the fact that the rotational tunneling modes go down with rising pressure.

References

[1] A.N. Heberlain and E.D. Adams, J. Low Temp. Phys. 3, 115 (1970). [https://link.springer.com/article/10.1007/BF00628321]
[19] M.A. White, J.A. Morrison, J. Chem. Phys. 72, 5927, (1980).
https://aip.scitation.org/doi/10.1063/1.439090

[20] M.A. White, J. Chem. Phys. 77, 1610 (1982).
https://aip.scitation.org/doi/10.1063/1.443946

[21] A. Hüller and J. Raich, J. Chem. Phys. 71, 3851 (1979).
https://aip.scitation.org/doi/10.1063/1.438795

[22] W. Press, M. Prager, A. Heidemann, J. Chem. Phys. 72, 5924 (1980).
https://aip.scitation.org/doi/10.1063/1.439089

[23] M. Prager, W. Press, A. Heidemann, J. Chem. Phys. 75, 1442 (1981).
https://aip.scitation.org/doi/10.1063/1.442151

[24] S. Buchman, W.T. Vetterling, D. Candela, R.V. Pound, Phys. Rev. B 26, 4826 (1982).
https://journals.aps.org/prb/abstract/10.1103/PhysRevB.26.4826

[25] D. Fabre, M.M. Thiery, K. Kobashi J. Chem Phys. 76, 4817 (1982).
https://aip.scitation.org/doi/10.1063/1.442800

[26] M.M. Thiery, D. Fabre, K. Kobashi, J. Chem. Phys. 83, 6165 (1985).
https://aip.scitation.org/doi/10.1063/1.449612

[27] P. Calvani, S. Lupi, P. Maselli, J. Chem. Phys. 91, 6737 (1989).
https://aip.scitation.org/doi/10.1063/1.457341

[28] P. Calvani, S. Lupi, Chem. Phys. Lett. 157, 11 (1989).
https://www.sciencedirect.com/science/article/abs/pii/0009261489871982

[29] M. Prager, W. Press, J. Chem. Phys. 92, 5517 (1990).
https://aip.scitation.org/doi/10.1063/1.458509

[30] M. Prager, W. Press, B. Asmussen, J. Combet, J. Chem. Phys. 117, 5821 (2002).
https://aip.scitation.org/doi/abs/10.1063/1.1503336

[31] A. Hüller, M. Prager, W. Press, T. Seydel, J. Chem. Phys. 128, 034503 (2008).
http://juser.fz-juelich.de/record/3/files/1.2822293.pdf

[32] A. Hüller, Phys. Rev. B 16, 1844 (1977).
https://journals.aps.org/prb/abstract/10.1103/PhysRevB.16.1844

[33] A.J. Nijman and N.J. Trappeniers, Chem. Phys. Lett. 47, 188 (1977).
https://www.sciencedirect.com/science/article/abs/pii/0009261477853372

[34] Physics of Cryocrystals. Editors: V.G. Manzhelii, Yu.A. Freiman, Michael L. Klein and Alexei A. Maradydin; AIP Press, Woodbury, New York, 1996.
https://www.springer.com/gp/book/9781563965371

[35] V.G. Manzhelii, A.I. Prokhvatinov, V.G.Gavrilko and A.P. Isakina, Structure and Thermodynamic Properties of Cryocrystals. Handbook. Begell House Ink. Publishers, NY, 1998.
https://www.begellhouse.com/books/structure-and-thermodynamic-properties-of-cryocrystals.html