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Tunnel splittings in solid CD₄ estimated from heat capacity data

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Heat capacity measurements have been made on CD₄, isotopically purified by gas chromatography, in the temperature region 0.15–4.0 K. For $T < 0.5$ K, the heat capacity is found to increase with decreasing temperature by much more than can be accounted for by contributions from impurities such as CHD₃. An analysis shows that the results can be reproduced by an array of low-lying tunneling states with maximum splitting of 0.042 ± 0.010 K. States in this region have been predicted by theory and found recently by measurements of inelastic neutron scattering. Enhanced thermal relaxation is observed in the calorimetric measurements in the region $T < 0.25$ K. The onset of conversion between nuclear spin symmetry species is a possible cause.

I. INTRODUCTION

Oriental ordering of the molecules in the solid isotopic methanes at low temperatures gives rise to complex arrays of energy states that correspond to librations and to rotational tunneling.¹ The low temperature structures of the solids (phase II or III) contain two or more sublattices^{2,3} and each methane has characteristic nuclear spin symmetry species.⁴ Thus, the quantitative prediction of the energy states to be observed for a particular methane presents considerable difficulty for theory. Recently, experimental observations of tunneling states in phase II of CH₄ (Ref. 1) have been used as a basis from which to predict^{5,6} the effect on tunneling of an isotopic shift to CD₄. The conclusion reached is that the tunnel splittings in CD₄ would be reduced by about a factor of 50 from those in CH₄ (~73 and 143 μ eV).

It is well known that closely spaced energy levels that are separated from other levels give rise to Schottky-type anomalies in heat capacities. Large such anomalies have been observed⁷⁻⁹ in the heat capacities of the partially deuterated methanes and shown to correspond to tunnel splittings in the range of 0.2 to 4 K (or 17 to 345 μ eV). These were easily characterized with calorimetric equipment capable of reaching a temperature of about 0.1 K. In view of this experience, it seemed worthwhile to stretch the capability of that equipment to see if tunneling states could be detected in CD₄ in the range predicted (3 to 6 μ eV), even though it might not be possible to analyze the anomaly fully.

The heat capacity of solid CD₄ was measured earlier¹⁰ down to a temperature of 0.3 K, but the specimen that was used contained at least 6.5% of impurities (O₂, N₂, and CHD₃). Their contributions to the heat capacity at low temperatures were so large that they obscured that of CD₄. In the experiments to be described, chemical and isotopic purification of the calorimetric specimen has been carried out so as to minimize that difficulty. On the other hand, it was only practicable to prepare a rather small specimen so that the heat capacity results have a limited accuracy—enough to detect the effects of

tunneling but not enough to characterize vibrational parameters of the CD₄ lattice.

II. EXPERIMENTAL

CD₄ that contained 3.4% of CHD₃ was obtained from Merck, Sharp, and Dohme in Montreal and was purified by preparative gas chromatography in a special column that has been fully described.^{8,11} The content of CHD₃ was reduced to 0.4 (± 0.2)% as determined by high resolution mass spectrometry. Before being filled into the calorimeter vessel to a pressure of about 1.5 atm, the specimen (7.63×10^{-3} mole) was exposed to a freshly prepared Misch metal getter to reduce the amount of O₂ impurity to a negligible level ($< 10^{-3}$ mole%). This was especially important because of the possible interference of a contribution to the heat capacity arising from the splitting of the ground electronic state of molecular oxygen.¹² Some N₂ was probably also removed by the getter.

The calorimetric measurements were made by the method used previously.^{7,11} The results, in order of their determination, are given in Table I. Those marked with a superscript "a" were obtained with a thermal shunt (6 cm of No. 36 AWG copper wire) connected between the calorimeter vessel and the mixing chamber of the dilution refrigerator. Its function was to facilitate the cooling of the specimen in the lowest temperature region. As far as could be discerned, it introduced no systematic errors.

III. RESULTS AND DISCUSSION

The heat capacities from the present and previous^{10,13} measurements are illustrated in Fig. 1. There appear to be large differences, but they need to be considered in relation to the purities and sizes of the specimens. As indicated earlier, the specimen used by Colwell¹⁰ contained 6.5% of impurities. The relatively large anomaly in its heat capacity is caused by 3.5% of CHD₃ and 1% of O₂.

The purest specimen is that used in the present work and the heat capacity results for it show reasonable precision, but good accuracy can only be claimed for them in the region $T < 1$ K. For instance, above $T = 3$ K, the

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TABLE I. Measured heat capacities of CD₄.

<i>T</i> (K)	10 ³ × <i>C_p</i> / <i>R</i>	<i>T</i> (K)	10 ³ × <i>C_p</i> / <i>R</i>
0.420	2.9	2.325	2.8
0.889	1.4	2.594	3.7
1.018	1.1	2.868	5.4
1.153	2.1	3.258	8.3
1.288	2.5	3.217	8.0
1.486	1.2	3.585	12
1.726	3.1	3.879	16
1.961	2.8	3.763	14
0.237	3.8	0.162	4.1 ^a
0.279	3.5	0.165	8.0 ^a
0.317	2.8	0.169	7.0 ^a
0.384	2.7	0.175	5.8 ^a
0.477	2.5	0.180	4.5 ^a
0.578	2.1	0.186	5.4 ^a
0.677	1.7	0.188	6.1 ^a
0.772	1.6	0.203	6.3 ^a
0.873	1.7	0.214	5.4 ^a
0.976	1.1	0.229	5.2 ^a
1.129	1.7	0.257	3.7 ^a
1.304	2.4	0.159	7.6 ^a
1.473	1.9	0.164	7.4 ^a
1.672	2.4	0.171	8.0 ^a
1.884	2.4	0.176	6.9 ^a
2.100	3.0	0.192	6.4 ^a

^aThermal shunt attached (see text).

CD₄ contributed only about 5% to the total heat capacity. Thus, the accuracy of the data in this region cannot be better than 20%. By contrast, the heat capacity contribution of the CD₄ at the lowest temperature was 40% of the total and so the observed anomalous rise in *C_p*/*R* for *T* < 1 K is well defined. The dashed curve indicates the contribution that would be made by 0.4% of CHD₃ based upon its known heat capacity.⁹ The position of the curve in relation to the experimental points for the present measurements shows that 0.4% is an upper bound on the amount of CHD₃ contained in the specimen.

The form of the heat capacity of an array of tunneling

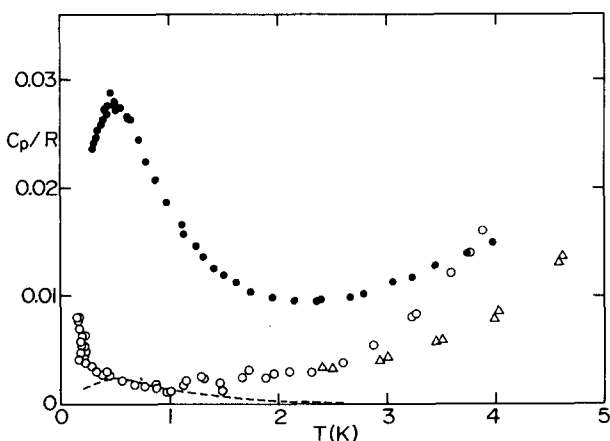


FIG. 1. Heat capacity of CD₄ as a function of temperature. (●) Colwell (Ref. 10); (Δ) Colwell, Gill, and Morrison (Ref. 13); (○) present measurements; (---) contribution from 0.4% of CHD₃.

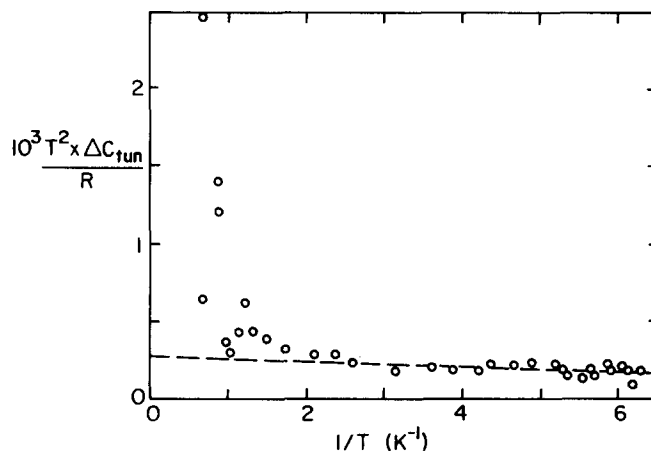


FIG. 2. Plot of $(T^2 \times \Delta C_{\text{tun}})/R$ vs $1/T$.

states is the same as that for the nuclear hyperfine heat capacity which, for sufficiently high (relative) temperatures, is¹⁴

$$C = A/T^2 + B/T^3 + C/T^4 + \dots \quad (1)$$

Here, the coefficients *A*, *B*, and *C* are related to the separation and degeneracies of nuclear spin states. To test the applicability of the expression, it is only necessary to plot $C \times T^2$ against $1/T$. The result should be a gentle curve that becomes a limiting straight line as $1/T \rightarrow 0$.

Before a fit to the present results could be attempted, it was necessary to subtract contributions to the heat capacity of CD₄ from impurity (assumed to be 0.2% of CHD₃) and from lattice vibrations. For the latter, the Debye approximation was assumed with a characteristic temperature corresponding to that estimated from the elastic constants of CD₄ (Ref. 15) (126 K). Thus is obtained the contribution of the tunneling states to the heat capacity.

$$\frac{\Delta C_{\text{tun}}}{R} = \frac{C_p}{R} - \frac{C(\text{lattice})}{R} - \frac{C(0.2\% \text{ CHD}_3)}{R} \quad (2)$$

Figure 2 is a plot of $(T^2 \times \Delta C_{\text{tun}})/R$ vs $1/T$. It is of the form to be expected [Eq. (1)]; the dashed line represents the first two terms and from it we get $A/R = 2.6 \times 10^{-4} \text{ K}^2$.

To extract any additional information, we are obliged to invoke a model for the manifold of tunneling states. The simplest is to assume a doublet which implies that *E* and *T* states in phase III of CD₄ are essentially degenerate, as has been suggested.¹⁶ Then, $\Delta C/R$ will be given by

$$\frac{\Delta C}{R} = \left(\frac{\delta}{T}\right)^2 \frac{g_0}{g_1} \frac{\exp(\delta/T)}{[1 + (g_0/g_1) \exp(\delta/T)]^2}, \quad (3)$$

where *g*₀ and *g*₁ are the degeneracies of the lower and upper states, respectively, δ is the energy separation, and

$$A/R = [g_0 g_1 / (g_0 + g_1)^2] \delta^2 \quad (4)$$

For CD₄, with degenerate *E* and *T* states, *g*₀ = 15 and *g*₁ = 66 (see Fig. 1 of Ref. 4), and so we find

$$\delta = 0.042 \pm 0.010 \text{ K} = 3.6 \pm 0.9 \text{ } \mu\text{eV}, \quad (5)$$

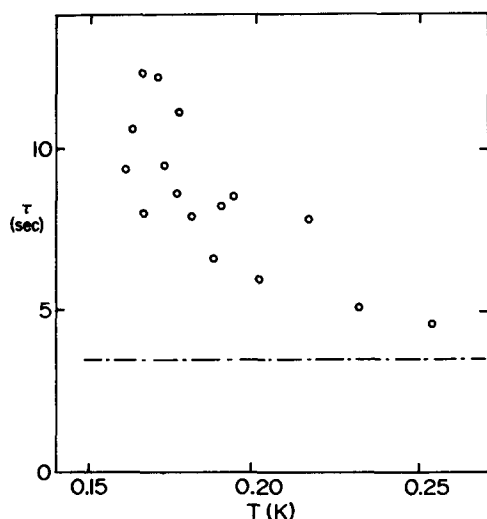


FIG. 3. Thermal relaxation after heating of the calorimeter vessel containing CD₄. (— · —) Relaxation time for the empty calorimeter vessel.

which includes an estimate of the overall uncertainty of the analysis except for that implicit in the assumption of only two energy states.

The measurements¹⁷ of inelastic neutron scattering in CD₄ at $T=4$ K report evidence for tunneling states at 1.2, 2.2, 2.8, and 3.4 μeV . It is very satisfying that the last of these agrees so well with result (5). The analysis of the heat capacity data which emphasizes the high temperature limiting form [Eq. (2)] should yield best an estimate of the largest tunnel splitting. We may therefore conclude that the occurrence of tunnel splittings in CD₄ significantly larger than $3.6 \pm 0.9 \mu\text{eV}$ is unlikely.

Finally, we note that, in the region $T < 0.3$ K, thermal equilibration of the calorimeter system containing CD₄ slowed significantly with decreasing temperature. This is illustrated in Fig. 3 where the thermal relaxation times from the experimental measurements are plotted as a function of temperature. No such change was detected^{8,9} with CH₂D₂ or CHD₃ in the calorimeter

vessel. On the other hand, with CH₃D, for which independent experiments had established that conversion between nuclear spin symmetry species was occurring,^{7,18} large and temperature-dependent thermal relaxation was observed.⁷ It is therefore possible that the results depicted in Fig. 3 indicate the onset of conversion in CD₄.

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