

**Oriental ordering and tunneling states in solid CH<sub>2</sub>D<sub>2</sub> as deduced from low temperature heat capacity and neutron cross section measurements**

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# Orientational ordering and tunneling states in solid CH<sub>2</sub>D<sub>2</sub> as deduced from low temperature heat capacity and neutron cross section measurements<sup>a)</sup>

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L8S 4M1

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Heat capacity measurements have been performed on isotopically purified solid CH<sub>2</sub>D<sub>2</sub> over the temperature range  $0.12 \leq T < 2.7$  K to characterize a large Schottky anomaly. In addition, the total neutron cross section of condensed CH<sub>2</sub>D<sub>2</sub> was measured over the temperature range  $0.75 \leq T \leq 100$  K. While a change in neutron cross section consistent with conversion between nuclear spin symmetry species was observed in the region  $T < 4.2$  K, no measurable thermal relaxation was encountered in the calorimetric experiments. On the basis of the latter result and of the magnitude of the entropy at the lowest temperatures, it is argued that conversion probably does not occur in this methane. It seems probable that the results should be interpreted as indicating incomplete orientational ordering of the CH<sub>2</sub>D<sub>2</sub> molecules in phase III. A model is developed for the manifold of low-lying tunneling states.

## I. INTRODUCTION

The preceding paper<sup>1</sup> describes thermal and neutron cross section experiments on solid CH<sub>3</sub>D. A similar study has been made of solid CH<sub>2</sub>D<sub>2</sub> and we report the results here. Earlier investigations<sup>2,3</sup> of the thermal properties of this isotopic methane were not carried to a sufficiently low temperature to define completely a Schottky anomaly in the heat capacity. Moreover, it was not known for certain whether conversion between the *A* and *B* nuclear spin symmetry species of CH<sub>2</sub>D<sub>2</sub> occurred.

The new thermodynamic results lead to the conclusion that conversion does not take place. As in the example of CH<sub>3</sub>D, the residual entropy of CH<sub>2</sub>D<sub>2</sub> is larger than that which corresponds to complete orientational ordering of the molecules. A scheme of tunneling levels is deduced for CH<sub>2</sub>D<sub>2</sub> which is more complicated than that proposed<sup>1</sup> for CH<sub>3</sub>D, mainly because conversion between the *A* and *B* species is not allowed. The scheme reproduces the measured heat capacities and calculated entropies well.

## II. EXPERIMENTAL

### A. Purification of the calorimetric methane sample

Commercially available deuteromethanes generally contain a few per cent of the other isotopic species (e. g., Table I) which can contribute significantly to measured thermodynamic properties at low temperatures. If heat capacities were to be additive, adequate corrections could be made to them. However, the tunneling states which cause the Schottky anomalies in the heat capacity may be greatly affected when one methane

is dissolved in another. In addition, there is the possibility that impurities may mask the behaviour of the pure material.<sup>4</sup>

The use of high efficiency packed columns in the chromatographic separation of methane isotopes has been demonstrated.<sup>5-7</sup> In the present experiments a column (120 m long, 6 mm o. d. copper tubing) packed with squalane-deactivated graphitized carbon black<sup>7</sup> was used. The column was operated at a temperature of 195 K, with the helium carrier gas at an inlet pressure of 400 psig. Samples [ $\sim 1$  ml STP of commercial CH<sub>2</sub>D<sub>2</sub> (Table I)] were injected through a rotary multiport valve. The difference in thermal conductivity between a pair of matched thermistors (one measuring the pure carrier gas and one measuring the eluted gas) was used for detection. Solenoid valves were used to divert the flow from the column to a trap maintained at a temperature of 77 K and packed with Porapak Q<sup>R</sup> (Waters Assoc., Framingham, MA) where the desired portion of the eluted sample was retained. With the trap at 77 K, the adsorbed helium was pumped off, and then the purified CH<sub>2</sub>D<sub>2</sub> sample was recovered on warming.<sup>6</sup>

Under optimum separation conditions, the retention time for CH<sub>2</sub>D<sub>2</sub> was 325 min. With a mixture of 40 parts of CH<sub>3</sub>D in 60 parts of CH<sub>2</sub>D<sub>2</sub>, the difference in retention times for the two isotopic species was determined to be about 3 min, with incomplete peak separation [Fig. 1 (a)]. Different portions of the eluted CH<sub>2</sub>D<sub>2</sub> sample were retained and analysed by mass spectrometry. The empirically-determined best separation was achieved by collecting the fraction indicated by the

TABLE I. Analysis of CH<sub>2</sub>D<sub>2</sub> samples (mole %).

Component	Commercial <sup>a</sup> CH <sub>2</sub> D <sub>2</sub>	Purified CH <sub>2</sub> D <sub>2</sub>
CH <sub>2</sub> D <sub>2</sub>	97.8 ± 0.2	99.0 ± 0.2
CH <sub>3</sub> D	2.2 ± 0.2	0.6 ± 0.2
CH <sub>4</sub>	≤ 0.2	...
O <sub>2</sub>	...	< 3 × 10 <sup>-4</sup>
N <sub>2</sub>	...	< 0.4

<sup>a</sup>Merck, Sharp, and Dohme, Montreal.

<sup>a)</sup>Taken in part from a thesis submitted by K. J. L. to McMaster University in partial fulfilment of the requirements for the Ph.D. degree (1977).

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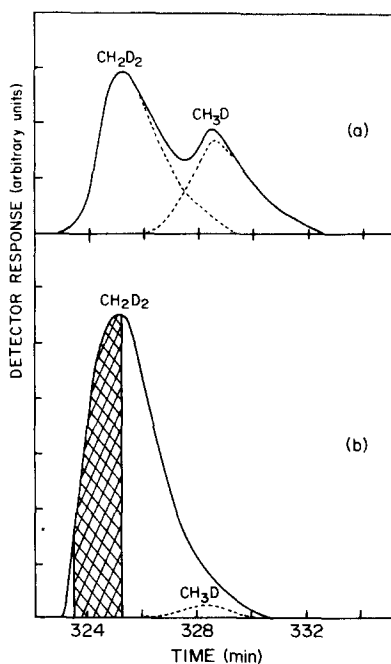


FIG. 1. Separation of methane isotopes: (a) 60:40 mixture of  $\text{CH}_3\text{D}$  in  $\text{CH}_2\text{D}_2$ ; (b) Separation of commercial  $\text{CH}_2\text{D}_2$ ; cross-hatched area represents fraction of eluted sample that was retained; dotted area indicates underlying peak due to  $\text{CH}_3\text{D}$  component.

cross-hatched area shown in Fig. 1 (b) which corresponds to about 40% of the injected sample. The column could be stacked by injecting every 12 min without interference between samples and, in this way, purified  $\text{CH}_2\text{D}_2$  was obtained at a rate of about 1 ml at STP per hour.

Small amounts of nitrogen and oxygen that were introduced in the sample handling procedure were removed in two stages. The isotopically purified sample was first rechromatographed using a procedure similar to that for isotopic purification with a 3 mm o.d. copper column, 37 m long and packed with 60/80 mesh Porapak  $Q^R$ . With the column at room temperature and the helium carrier gas at an inlet pressure of 210 psig, samples of  $\sim 8$  ml at STP had retention times of 12 and 15 min for air and  $\text{CH}_2\text{D}_2$ , respectively, with good peak separation. The  $\text{CH}_2\text{D}_2$  was again collected on a cold Porapak  $Q^R$  trap.

The sample was then introduced into a diffuse-layer Misch metal getter to remove more  $\text{O}_2$  and  $\text{N}_2$ . A thin film of this cerium-lanthanum alloy has been shown<sup>8</sup> to be effective in reducing the oxygen content in methane samples to less than 3 ppm. The sample was left in contact with the getter overnight and the nitrogen content was reduced from 2% to  $\leq 0.4\%$ . The small contribution of the nitrogen to the heat capacity of the sample was corrected for in a straightforward manner.<sup>3</sup>

The mass analysis (Table I) was performed at the University of Toronto on a modified EMI-52 magnetic-deflection, single-focusing mass spectrometer. The electron beam energy was reduced until a constant 17:18 mass ratio was obtained. At this energy ( $\sim 8$  eV), the mass 18 peak was due entirely to  $\text{CH}_2\text{D}_2^+$  and the 17 mass

peak to  $\text{CH}_3\text{D}^+$ . Analyses for  $\text{N}_2$  and  $\text{O}_2$  were not made because of the background in the mass spectrometer.

### B. Calorimetric measurements

The heat capacity of 0.002594 mole of isotopically purified  $\text{CH}_2\text{D}_2$  was measured over the temperature range  $0.12 \leq T \leq 2.7$  K. The calorimetric method is described fully in the preceding paper.<sup>1</sup> One modification was made to the calorimeter assembly for some of the measurements in the range  $T < 0.36$  K because of the great importance of achieving as low a temperature as possible<sup>9</sup> in order to characterize the Schottky anomaly. A thermal link (6.5 cm of #36 AWG copper wire) was attached between the calorimeter vessel and the mixing chamber of the dilution refrigerator. It did not contribute significantly to the heat capacity. While the increased heat exchange between the calorimeter vessel and its surroundings decreased the precision of the measurements, the results agreed well with those obtained without the link in the temperature range of overlap.

### C. Neutron cross section measurements

The neutron cross section measurements were performed as described previously for  $\text{CH}_4$ <sup>10</sup> and  $\text{CH}_3\text{D}$ <sup>1</sup> and no further description of the method is necessary here. In the methanes, the sensitivity of the neutron cross section technique for the determination of spin species composition depends upon the change in cross section that accompanies a change in the spin state of the protons. Since  $\text{CH}_2\text{D}_2$  has fewer protons per molecule, it follows that the technique is less sensitive for this methane.

Because of the large sample size ( $\sim 0.1$  mole) required for the neutron cross section measurements, it was only practicable to use commercially available  $\text{CH}_2\text{D}_2$  without isotopic purification. The content of air was reduced by trap to trap distillation at  $T = 77$  K, which should have decreased the oxygen concentration to less than 100 ppm.

## III. RESULTS

### A. Thermal measurements

The primary heat capacity data are given in Table II and displayed in Fig. 2. Curvature corrections<sup>11</sup> as well as a correction for the  $\text{CH}_3\text{D}$  impurity were applied to the data. The contribution of the methane to the total heat capacity varied between 95% and 35% from the lowest to the highest temperature. The present results are significantly different from those obtained earlier for  $\text{CH}_2\text{D}_2$ .<sup>3</sup> The difference is particularly large in the region  $T \geq 1.0$  K ( $\sim 45\%$  at  $T = 2.0$  K), and is much outside the combined uncertainties of the two sets of measurements. A similar discrepancy appears in the comparison of results for  $\text{CH}_3\text{D}$  and, as has been noted<sup>1,12</sup>, it cannot be attributed to systematic errors in the experiments.

The fact that the discrepancy was larger for the smaller specimen used here<sup>13</sup> led us to investigate the effect of the sample configuration on the measured heat capacity. As is reported elsewhere<sup>14</sup>, the heat capacities of small amounts of argon were measured over the same temperature range and revealed a large contribution to

TABLE II. Measured heat capacity of the CH<sub>2</sub>D<sub>2</sub> sample.

$T$ (K)	$C_p/R$	$T$ (K)	$C_p/R^a$
0.720	0.373	0.164	0.647
0.284	0.900	0.136	0.485
0.331	0.816	0.160	0.582
0.387	0.696	0.186	0.673
0.498	0.531	0.210	0.811
0.660	0.409	0.230	0.838
0.861	0.308	0.242	0.869
1.051	0.248	0.257	0.900
1.223	0.211	0.361	0.770
1.404	0.183	0.295	0.895
1.588	0.153	0.262	0.882
1.766	0.130	0.198	0.748
1.952	0.114	0.199	0.735
2.181	0.097	0.145	0.510
2.441	0.081	0.169	0.577
2.677	0.067	0.194	0.742
0.228	0.903	0.217	0.831
0.261	0.914	0.230	0.906
0.291	0.877	0.238	0.893
0.324	0.826		
0.356	0.752		
0.388	0.701		
0.419	0.641		
1.398	0.182		
1.425	0.176		
1.447	0.175		
0.961	0.281		
1.154	0.228		
1.346	0.192		
1.535	0.156		
1.726	0.134		
1.915	0.116		
2.097	0.101		
0.941	0.281		
1.117	0.238		
1.306	0.198		
1.507	0.162		
1.712	0.133		
1.914	0.117		
2.112	0.098		

<sup>a</sup>Measurements made with copper wire link attached.

the heat capacity that was a linear function of temperature and inversely proportional to the size of specimen. Smoothed values of the heat capacity of CH<sub>2</sub>D<sub>2</sub> were corrected for the "size" effect

$$\Delta C_p = -0.163T \text{ J/mole deg}$$

and are given in Table III. They agree well with Colwell's estimates of the heat capacity of "pure" CH<sub>2</sub>D<sub>2</sub> for  $T > 0.7$  K. This is very significant because Colwell's specimen contained 0.11% of O<sub>2</sub> while ours had been treated with a getter to remove O<sub>2</sub> to the level of < 3 ppm.

No relaxation effects were observed in the thermal measurements. Thermal equilibrium after heating was achieved within less than 5 s. This is in contrast to Colwell's observations<sup>3</sup> but it should be noted that his specimen contained 5.2% of CH<sub>3</sub>D. It seems probable now that the relaxation he found should be ascribed to nuclear spin conversion in that impurity.

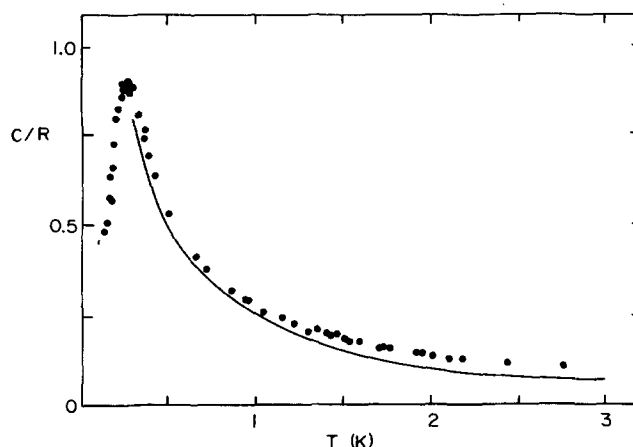


FIG. 2. The low temperature heat capacity of CH<sub>2</sub>D<sub>2</sub>: ● = present work; — = smoothed values.<sup>3</sup>

The absence of observable thermal relaxation indicates that conversion does not occur in CH<sub>2</sub>D<sub>2</sub> on the time scale of the calorimetric experiments. It should also be mentioned that the specimen was kept at temperatures of 4 K or less for periods of more than two weeks. No change in heat capacity was detected in this time thus indicating that slow conversion probably does not occur either. The possibility of very fast conversion ( $\tau \ll 1$  s) cannot be ruled out. However, as will be discussed in Sec. IV. (C), such a possibility is inconsistent with deductions from the entropy.

### B. Neutron cross section measurements

The neutron scattering experiments were carried out on CH<sub>2</sub>D<sub>2</sub> at low temperatures ( $T < 4$  K) to check for

TABLE III. Smoothed values of the heat capacity of pure CH<sub>2</sub>D<sub>2</sub>.<sup>a</sup>

$T$ (K)	$C_p/R$
0.14	0.493
0.16	0.586
0.18	0.681
0.20	0.781
0.22	0.878
0.24	0.905
0.26	0.907
0.28	0.897
0.30	0.871
0.35	0.773
0.40	0.684
0.45	0.604
0.50	0.528
0.60	0.449
0.70	0.380
0.80	0.331
0.90	0.294
1.00	0.264
1.50	0.164
2.00	0.108
2.50	0.076
3.00	0.053

<sup>a</sup>Corrected for "size" effect.

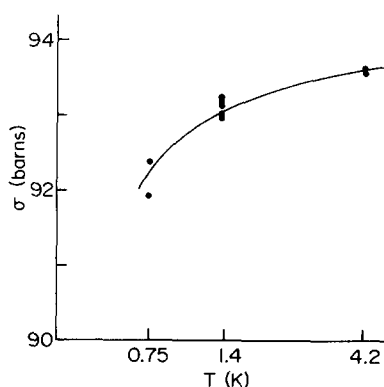


FIG. 3. The total neutron cross section of  $\text{CH}_2\text{D}_2$  as a function of temperature.

nuclear spin conversion in this methane by an independent method. Some measurements were made at higher temperatures for purposes of comparison with the results for  $\text{CH}_4$ <sup>10</sup> and  $\text{CH}_3\text{D}$ <sup>1</sup>. The low temperature results for  $\text{CH}_2\text{D}_2$  are shown in Fig. 3. The notable feature is that the temperature dependence of the cross section is opposite to that found for  $\text{CH}_4$  or  $\text{CH}_3\text{D}$ . This is consistent with the direction of change expected for conversion in  $\text{CH}_2\text{D}_2$ . Whereas, for  $\text{CH}_3\text{D}$ ,  $\langle I(I+1) \rangle$  for protons should increase from 2.25 to 3.75 for complete conversion to the *A* nuclear spin symmetry species, it should decrease from 1.5 to 1.2 for the similar conversion in  $\text{CH}_2\text{D}_2$ .<sup>15</sup> No time-dependent cross sections were observed in the neutron experiments but the counting intervals were necessarily rather long because of the lower sensitivity of the measurements on  $\text{CH}_2\text{D}_2$ . Nevertheless, the results place an upper limit of 3 min on the characteristic lifetime of any conversion processes.

#### IV. DISCUSSION

##### A. Restriction of molecular orientation

Figure 4 shows a plot of the total neutron cross section as a function of temperature for  $\text{CH}_4$ ,  $\text{CH}_3\text{D}$ , and  $\text{CH}_2\text{D}_2$ . The data have been normalized at  $T = 95$  K to facilitate comparison. The similarity of the three curves is striking. The large discontinuity at the triple point ( $T \approx 90$  K) primarily reflects a decrease in the translational motion of the molecules on solidification, since, in the methanes, there is known to be relatively little change in rotational freedom at the melting point<sup>16</sup>. This abrupt change in cross section is probably associated with a decreased density of low energy translational states in the solid, which in turn reduces the number of possible inelastic scattering processes. The magnitude of the decrease in cross section at the triple point is the same, within the experimental error, for all three methanes. Similar discontinuities in total neutron cross section have been observed in other molecular solids at their triple points,<sup>17,18</sup> and, in ammonium iodide, at a first order phase transition ( $T = 263$  K) in which the  $\text{NH}_4^+$  ion goes from a hindered rotor to a nearly free rotor.<sup>19</sup>

Between the triple point and  $T = 50$  K,  $\sigma$  decreases almost linearly with decreasing temperature. This behavior is characteristic of the cross section for a free rotor in which the possible number of energy gain

scattering processes decreases as higher energy states depopulate. It is exemplified by a calculation of the temperature dependence of the cross section of methane based upon a free rotor model.<sup>20</sup> The result is displayed as a dashed line in Fig. 4. The assumptions of this classical calculation limit its validity, in the methane system, to relatively high temperatures and high neutron energies such that the neutron scattering can be approximated by classical arguments.

Below  $T \approx 50$  K, the slope of  $\sigma$  vs  $T$  begins to decrease until, in the region just above the phase I to II transition, it becomes essentially zero. Such behavior of the cross section is consistent with increased restriction of rotational motion, associated with the strengthening of the orientational correlation,<sup>21</sup> which ultimately leads to a long range orientational order on six of the eight sublattices of phase II.<sup>22</sup>

Another interesting feature of the data shown in Fig. 4 is the trend with increasing deuterium substitution of the methane. At the triple point, all three methanes exhibit similar behavior but, at lower temperatures, the  $\sigma$  vs  $T$  curves for the three isotopes have significantly different slopes. The reason for the effect is probably the same as that which is used to explain the observed trend in the upper transition temperature with deuteration.<sup>23</sup> The transition temperatures are found to scale to a rotational temperature that is directly related to the moments of inertia of the molecules. As the moment of inertia increases, the energy level spacings decrease and so the rate of depopulation of the levels with temperature also decreases. Thus, the slope of the  $\sigma$  vs  $T$  curves should be less for the more highly deuterated methanes, as is observed.

Because of the lower sensitivity of the measurements of the neutron cross section of  $\text{CH}_2\text{D}_2$ , it was not possible to obtain any information about the order of the phase transitions. The measurements on  $\text{CH}_3\text{D}$  described in the preceding paper,<sup>1</sup> brought out a significant difference between the III  $\rightarrow$  II and II  $\rightarrow$  I transitions.

##### B. The entropy of $\text{CH}_2\text{D}_2$

At  $P = 0.1079$  atm and  $T = 90.17$  K, the entropy of  $\text{CH}_2\text{D}_2$  in the gas state, as calculated by statistical thermodynamical methods and including nuclear spins,

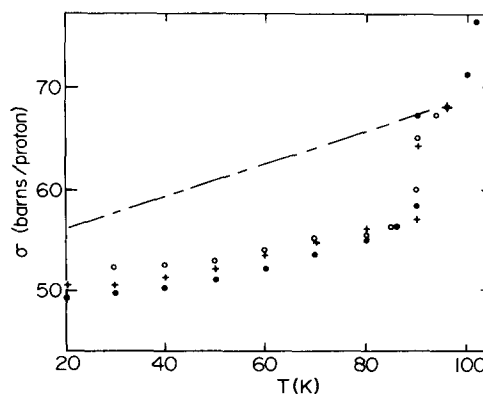


FIG. 4. The neutron cross section per proton for phase I of three methanes:  $\bullet = \text{CH}_4$ ;  $+$  =  $\text{CH}_3\text{D}$ ;  $\circ = \text{CH}_2\text{D}_2$ ;  $-$  = Krieger-Nelkin calculation.<sup>19</sup>

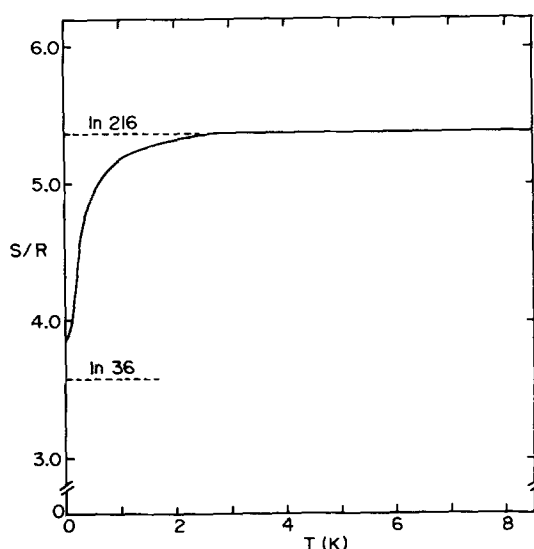


FIG. 5. The entropy (including nuclear spin) of solid CH<sub>2</sub>D<sub>2</sub> as a function of temperature.

is  $25.91 (\pm 0.03)R$ . The entropy of solid CH<sub>2</sub>D<sub>2</sub> as a function of temperature can be obtained from this result by subtracting entropy decrements (from calorimetric data published previously<sup>2,3</sup> as well as those given here). The result is illustrated in Fig. 5.

We estimate the entropy of CH<sub>2</sub>D<sub>2</sub> at  $T=0$  K by extrapolation from two temperature regions:

- (i)  $8 \leq T \leq 15$  K, and
- (ii)  $0.12 \leq T \leq 0.3$  K.

If it is assumed that, for (i),

$$S(P, T) = S_0 + aT^3 \quad (1)$$

we find

$$S_0/R = 5.36 \pm 0.10. \quad (2)$$

On the other hand, extrapolation through region (ii), on the assumption that the heat capacity goes smoothly to zero for  $T < 0.12$  K (the starting temperature of the lowest thermal measurement), leads to

$$S_0/R = 3.81 \pm 0.10. \quad (3)$$

Within the limits shown, Results (2) is equal to

$$\ln(2^2 \times 3^2 \times 6) = \ln 216 = 5.38, \quad (4)$$

which included the full contributions of the proton and deuteron spins and of orientational disorder of the molecules on the lattice sites. Thus, at  $T=8$  K, no conversion between nuclear spin symmetry species has occurred and the molecules can reorient easily within the time of a thermodynamics experiment.

Result (3) is not so easy to interpret. The apparent zero point entropy due to complete ordering without spin conversion is  $R\ln 36 = 3.58R$ , while for complete ordering and complete conversion, it is  $R\ln 15 = 2.7R$ . Complete conversion to the *A* species without ordering would give an apparent zero point entropy of  $R\ln 90 = 4.50R$ . Obviously, none of these agrees with Result (3). It is clear, however, that the apparent zero point entropy is too large to account for a low temperature

structure of completely oriented molecules, with or without nuclear spin conversion.

### C. Tunneling states for CH<sub>2</sub>D<sub>2</sub>

In analyzing the results for CH<sub>2</sub>D<sub>2</sub> so as to derive an estimate of the array of tunneling states, we are faced with a dilemma. The neutron cross section data suggest that conversion is occurring, but, on the other hand, no thermal relaxation of the kind that characterizes conversion in CH<sub>4</sub><sup>24,25</sup> and CH<sub>3</sub>D<sup>1,3</sup> was observed. If we were to assume that conversion were so rapid that its thermal consequences could not be observed under the conditions of the calorimetric experiments, the entropy change to be ascribed to orientational ordering would be  $(5.36 - 3.81 - \ln 216/90)R = 0.67R$ . This is to be compared with  $(4.60 - 2.63 - \ln 2)R = 1.28R$ , which is the corresponding entropy change for CH<sub>3</sub>D.<sup>1</sup> To put these on an equivalent basis, we have

$$\text{for CH}_2\text{D}_2, \quad \frac{0.67R}{R\ln 6} = 0.38$$

$$\text{and, for CH}_3\text{D}, \quad \frac{1.28R}{R\ln 4} = 0.92.$$

It seems extremely unlikely that the ordering processes in CH<sub>2</sub>D<sub>2</sub> and CH<sub>3</sub>D would differ by as much as these entropy differences imply.

If we assume that there is complete conversion in CH<sub>3</sub>D and none in CH<sub>2</sub>D<sub>2</sub>, the entropy changes to be associated with orientational ordering become  $(4.60 - 2.63 - \ln 2)R = 1.28R$  and  $(5.38 - 3.81)R = 1.57$ , respectively. On an equivalent basis, for CH<sub>2</sub>D<sub>2</sub>,

$$\frac{1.57R}{R\ln 6} = 0.88$$

and, for CH<sub>3</sub>D,

$$\frac{1.28R}{R\ln 4} = 0.92.$$

These are much more in line with an expectation that the deuterated methanes would behave similarly, as evidenced by the modest shifts of transition temperatures with the amount of deuteration.<sup>23</sup> Of course, partial conversion of CH<sub>2</sub>D<sub>2</sub> on one type of sublattice might happen but this seems improbable. We are thus led to the conclusion that there is another explanation for the neutron results. The decrease in cross section for  $T < 4.2$  K could arise from a change in the inelastic scattering of the neutrons as the low-lying states depopulate at the lowest temperatures.

In the preceding paper,<sup>1</sup> both experimental<sup>18,25-27</sup> and theoretical<sup>28,29</sup> evidence was cited that the energy states of the molecules of the two different sublattices of phase II of CH<sub>4</sub> differed considerably. An energy level scheme was then derived for CH<sub>3</sub>D in phase III, based on a model of two types of sublattice, even though there is theoretical evidence<sup>30</sup> that three types of sublattice may be present in phase III. We shall now derive a philosophically similar model for the tunneling states in phase III of CH<sub>2</sub>D<sub>2</sub> on the assumption that no conversion occurs between the *A* and *B* nuclear spin symmetry species.

For reasons given in the discussion of the example of CH<sub>3</sub>D,<sup>1</sup> we assume the two sublattice arrays to be in

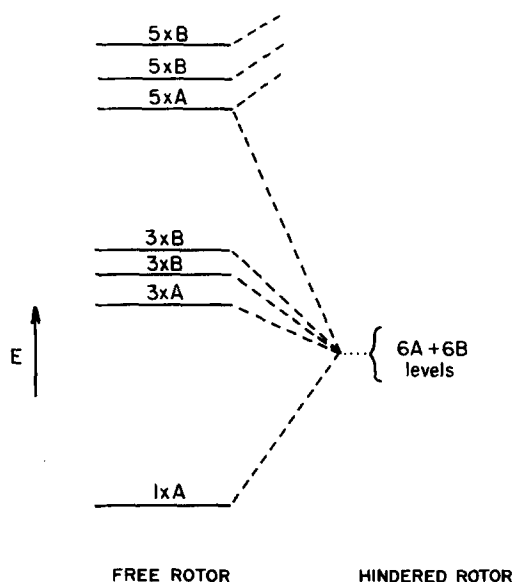


FIG. 6. Schematic representation of the perturbation of the lowest rotational energy levels of CH<sub>2</sub>D<sub>2</sub>. The A and B rotational levels have spin weights of 15 and 21, respectively. The positions of the free rotor levels are not to scale.

the proportions 25:75. The derived set of energy levels must be consistent with the following:

(i) the apparent residual entropies [Eqs. (2) and (3)] given in the preceding subsection, and

(ii) the heat capacity as a function of temperature. Group theory<sup>2,31</sup> indicates for CH<sub>2</sub>D<sub>2</sub> that there should be (Fig. 6) a total of six A and six B closely-spaced rotational energy levels, with nuclear spin degeneracies of 15 and 21, respectively. This would give rise to a total of 216 states per sublattice array, or an apparent residual entropy  $S_0/R = \ln 216$ , in agreement with Eq. (2). To account for the apparent residual entropy obtained by extrapolation at lower temperatures [Eq. (3)], a total of four energy arrays (those associated with each of the A and B molecules on both the 25% and the 75% sublattices) must be considered.

Thus,

$$\frac{S_0}{R} = \frac{1}{4} \left[ \frac{90}{216} \ln g_A^o + \frac{126}{216} \ln g_B^o \right] + \frac{3}{4} \left[ \frac{90}{216} \ln g_{A^*}^o + \frac{126}{216} \ln g_{B^*}^o \right] - \frac{90}{216} \ln \frac{90}{216} - \frac{126}{216} \ln \frac{126}{216}, \quad (5)$$

where  $g_A^o$ , and  $g_B^o$  and  $g_{A^*}^o$ ,  $g_{B^*}^o$  are the apparent ground state degeneracies of the molecules on the assumed 25% and 75% sublattices, respectively.

Since the nuclear spin degeneracy of an A level is 15,  $g_A^o$  and  $g_{A^*}^o$  must be integral multiples of 15. Similarly,  $g_B^o$  and  $g_{B^*}^o$  must be multiples of 21. In contrast to the example of CH<sub>3</sub>D, where only one set of ground state degeneracies could satisfy the apparent residual entropy, the four different ground states for CH<sub>2</sub>D<sub>2</sub> give rise to 22 possible sets of apparent ground state degeneracies. Of these, four sets resembled the CH<sub>3</sub>D array, in that

TABLE IV. Some possible ground state degeneracies for CH<sub>2</sub>D<sub>2</sub>.

	$g_A^o$	$g_B^o$	$g_{A^*}^o$	$g_{B^*}^o$	$S_0/R$
(a)	30	42	15	21	3.76
(b)	30	63	15	21	3.82
(c)	30	84	15	21	3.86
(d)	30	105	15	21	3.90

the ground state degeneracy  $g_{A^*}^o$  was that due to the nuclear spin degeneracy, while  $g_A^o$  was twice the nuclear spin degeneracy. These four sets are listed in Table IV along with their corresponding residual entropies.

Group theory shows<sup>31</sup> that, in a tetrahedral field, the six B levels of CH<sub>2</sub>D<sub>2</sub> split into two sets of three levels, each with a total degeneracy of 63. A less symmetrical field would presumably reduce the degeneracy to give six levels, each with the nuclear spin degeneracy of 21. This general line of argument gives a preference to example (b) in Table IV.

The ground state degeneracies of (b) and the total number of states in each array as predicted by group theory were used to determine the energies of the remaining levels by a nonlinear least squares fit to the experimental low temperature heat capacity. The energy level scheme is illustrated in Fig. 7. The agreement with the experimental heat capacities is excellent (Fig. 8).

In contrast to the example of CH<sub>3</sub>D, the absence of nuclear spin conversion in CH<sub>2</sub>D<sub>2</sub> makes the relative energies of the A and B levels indeterminate. However, there cannot be any degeneracy between an A and a B level as this would lead to facile conversion.

The arrays of energy states for the A and B molecules give different views of the consistency of the model used. For example, on the one hand,  $g_B^o/g_{B^*}^o = 2$ , which is consistent with the smaller splitting deduced for B

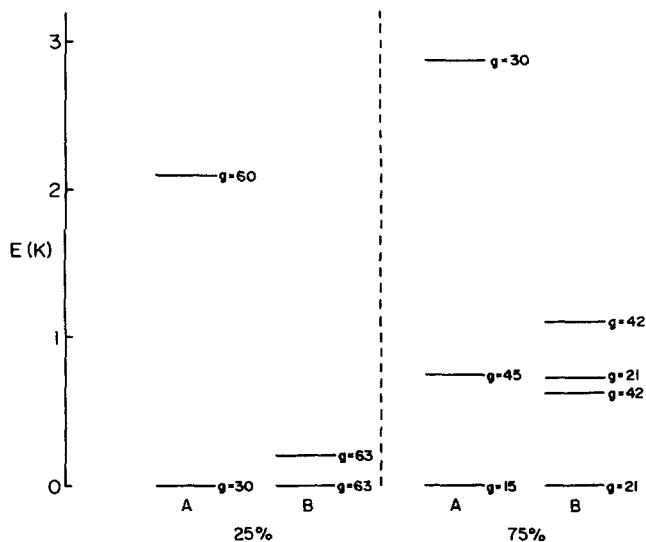


FIG. 7. Derived tunneling states for phase III of CH<sub>2</sub>D<sub>2</sub>. The degeneracies include the rotational contribution and the nuclear spin contributions of the protons and the deuterons.

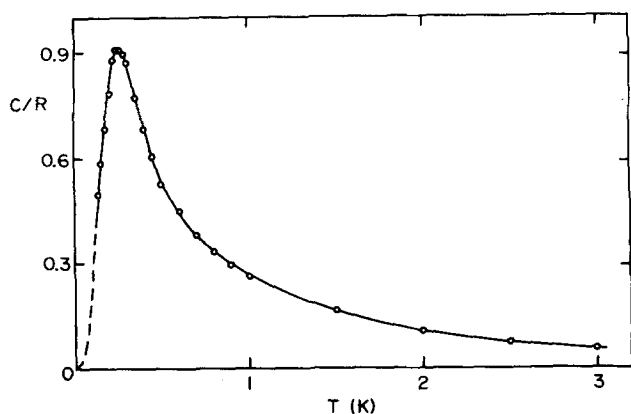


FIG. 8. The Schottky anomaly in CH<sub>3</sub>D. o =  $C_p/R$  (Table III),  $C/R$  (lattice); - = calculated from energy levels of Fig. 7.

molecules on sites in the 25% sublattice. On the other hand, an implicit assumption of the model is that the crystalline field is less for the 25% sublattice.<sup>30</sup> A similar type of argument based on the A molecules also reveals inconsistencies. Their resolution requires some direct probing of some of the energy states, as was concluded from the study of CH<sub>3</sub>D.

In summary, the present results indicate that, at the lowest temperature reached ( $T=0.12$  K), solid CH<sub>2</sub>D<sub>2</sub> is not completely orientationally ordered. CH<sub>3</sub>D behaves in a similar manner,<sup>1</sup> except that conversion between the nuclear spin symmetry species appears to go to completion in it. Investigation of the mechanism of conversion in CH<sub>3</sub>D might lead to an explanation of why conversion does not seem to occur in CH<sub>2</sub>D<sub>2</sub>. Colwell's measurements of the heat capacity of CHD<sub>3</sub> were regrettably not made to a low enough temperature to allow firm conclusions to be reached about orientational ordering and spin conversion in that methane. It would be valuable to extend those measurements. In addition, a determination of the structure of phase III of the deuteromethanes, as well as a direct determination of the low-lying energy states (by neutron scattering or level-crossing experiments), would significantly improve our understanding of the quantum behaviour of these solids.

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