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Deductions about the structure of phase III from thermodynamic measurements on solid isotopic methanes

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L8S 4M1

In a continuing study of the solid isotopic methanes, the heat capacity of solid CHD_3 has been measured in the range $0.15 < T < 3$ K. Some structure is found in a Schottky anomaly in the region of the measurements and it is related to the composition of nuclear spin symmetry species in the solid. There is no evidence of spin conversion. The entropy of CHD_3 has been calculated as a function of temperature from the heat capacity and other data, and is used to make deductions about quantum disorder in the solid. Combined results for CH_3D, CH_2D_2 and CHD_3 lead to the conclusion that the structure of phase III of solid methane is quantum disordered and that it must contain at least three types of sublattice. A model consisting of two sublattices with tetrahedral molecular fields and one with symmetry lower than tetrahedral, accounts for the experimental observations satisfactorily.

I. INTRODUCTION

The extensive studies of the properties of solid methane that are being made have as their object the delineation of the energy states of the molecules in the three known solid phases. The current state of understanding of solid CH_4 is well summarized in a recent article.[1] The structures of two of the phases which it forms (phases I and II) are known[2,3] and provide the basis for the interpretation of NMR,[4] calorimetric,[5] neutron scattering,[6] and optical[7,8] measurements in terms of rotational, librational, and tunneling states. While a small amount of structural information has been obtained[9] for the lowest temperature phase III, which all of the deuterated methanes form under vapor pressure but CH_4 forms only for $P > 0.2$ kbar, severe experimental difficulties will probably rule out a full structural determination being made soon by either x-ray or neutron diffraction. Thus, for the present, the characterization of the structure must be undertaken by indirect means.

Detailed analyses[10,11] of the heat capacities and entropies of the partially deuterated methanes CH_3D and CH_2D_2 led to the conclusion that phase III must contain a minimum of two types of sites for the molecules. In a comprehensive theoretical study,[12] a model potential that takes account of interactions up to hexadecapole–hexadecapole has been used to derive stability conditions for the different solid phases of methane. A probable space group $P4_2/mbc$ with 16 molecules per unit cell is proposed for phase III. It is related to the known structure of phase II by the changes of site symmetries from O and D_{2d} (phase II) to D_2, S_4, and C_s (phase III). The proposed structure is now being tested through measurements of infrared[13] and Raman spectra.[14]

The thermodynamic measurements on the third partially deuterated methane CHD_3, to be described in this paper, were undertaken with the hope that results for it could be used to gain further insight into the structure of phase III. That hope has been borne out in that the residual entropy of CHD_3, now much more accurately

determined than heretofore, provides a key for producing a consistent set of site symmetries that accounts for the measured thermodynamic properties of all three partially deuterated methanes: CH_3D, CH_2D_2, and CHD_3. The corresponding model differs somewhat in detail from that derived from theory[12] but, in agreement with the theoretical model, it invokes three types of sites.

No evidence is found for conversion between nuclear spin symmetry species of CHD_3. That plus the occurrence of some structure in the heat capacity of the solid in the region $T < 0.5$ K allows some reasonably firm deductions to be made about the lowest-lying tunneling states.

II. EXPERIMENTAL

A. Specimen purification and analysis

Commercially available CHD_3 (Merck, Sharp and Dohme, Montreal) was isotopically purified with a special gas chromatographic column by a technique that has been described previously.[11] Isotopic analysis was performed with a mass spectrometer and the results are given in Table I. Before the calorimetric specimen (0.003367 mole) was sealed in the calorimeter vessel, it was exposed to a freshly prepared Misch metal getter which is known[15] to reduce the O_2 content of methane to < 3 ppm.

B. Calorimetry

The technique of calorimetry, including the establishment of the temperature scale, has been fully described.[10] Heat capacity measurements were made on

TABLE I. Analyses of CHD_3 samples (mole%).

	Commerical	Isotopically purified
CHD_3	≥ 94.6	99.4 ± 0.2
CH_2D_2	≤ 5.4	0.6 ± 0.2
O_2	$\cdots$	$< 3 \times 10^{-4}$

TABLE II. Measured heat capacities of CHD$_3$.

T (K)	C_p/R	T (K)	C_p/R
0.402	0.556	0.562	0.560
0.453	0.581	0.597	0.536
0.496	0.590	0.636	0.517
0.536	0.574	0.677	0.491
0.581	0.548	0.732	0.447
0.598	0.543	0.794	0.393
0.637	0.506	0.841	0.369
0.685	0.476	0.308	0.459
0.734	0.450	0.355	0.520
0.792	0.411	0.404	0.568
0.851	0.367	0.456	0.577
0.905	0.341	0.503	0.577
1.002	0.304	0.191	0.311
1.027	0.280	0.219	0.340
1.075	0.253	0.248	0.383
0.996	0.290	0.276	0.419
1.105	0.247	0.315	0.463
1.227	0.205	0.357	0.523
1.360	0.173	0.388	0.550
1.531	0.140	0.168	0.290
1.737	0.110	0.197	0.319
1.950	0.088	0.228	0.355
2.201	0.071	0.260	0.393
2.476	0.061	0.291	0.437
2.764	0.048	0.323	0.486
0.495	0.591	0.358	0.524
0.529	0.571		

the specimen of CHD$_3$ for temperatures between 0.15 and 3 K. No unusual effects such as anomalous thermal relaxation were observed. As far as could be determined, thermal equilibrium within the calorimeter vessel was established within a second or two after heating. In this respect, the behavior of the calorimeter assembly was the same as that for the measurements on CH$_2$D$_2$.[11] By contrast, for CH$_3$D, in which conversion between nuclear spin symmetry species was shown to occur,[10] thermal relaxation with a characteristic half-life of 1 to 2 min was found.

Most of the measurements for $T < 0.5$ K were made with a thermal shunt (6.5 cm of #36 AWG copper wire) connected between the calorimeter vessel and the mixing chamber of the helium dilution refrigerator. This increased the rate of cooling of the calorimeter vessel but not to the extent that it decreased the accuracy with which the heat capacity measurements could be made. In the region $0.5 < T < 0.9$ K, the observed thermal conductance could be fitted to the simple expression

$$h = 0.2T^4 \quad (\text{W cm}^{-2}\,\text{K}^{-1}) . \tag{1}$$

It is similar to that which has been reported[16] for boundary-limited conductance for a junction of superconducting tin to copper:

$$h = 0.11T^3 \quad (\text{W cm}^{-2}\,\text{K}^{-1}) , \tag{2}$$

or of superconducting lead to copper:

$$h = 0.09T^4 \quad (\text{W cm}^{-2}\,\text{K}^{-1}) . \tag{3}$$

III. RESULTS

The measured heat capacities are listed in Table II in order of their determination. They include data for

three coolings from room temperature; the three sets are indistinguishable. Also, as mentioned above, no anomalous thermal relaxation was observed, nor was there any significant change of the heat capacity when the calorimeter system was kept at temperatures below 4 K for up to a week. We conclude from this that conversion between the A and E nuclear spin symmetry species is either very fast ($\tau_{1/2} <$ a fraction of a second) or so slow as to be immeasurable in a calorimetric experiment. The methane specimen used here was very pure and it is legitimate to ask if the conversion might not be appreciable in the presence of O$_2$, which affects conversion in CH$_4$ drastically[17] and in CH$_3$D to a measurable extent.[10] A comparison of the present heat capacity results for CHD$_3$ with some obtained earlier indicates that that is not the case.

Two previous sets of results are available for comparison. One[18] was obtained for CHD$_3$ containing 9% of other deuterated methanes and the other[19] for a specimen containing 4.6% total of CH$_2$D$_2$, CD$_4$, O$_2$, and N$_2$ impurities. Before a proper comparison can be made, purity corrections are therefore necessary to the earlier results. In addition, a correction, earlier thought to be a size effect,[20] was made to the heat capacity of the calorimeter and its contents:

$$\Delta C_p/R = 0.015T . \tag{4}$$

After such treatments, the results in Table II and those of Colwell[19] are compared in Fig. 1. The agreement is within the combined accuracies of the two sets of results and of the corrections, except in the region $T < 0.6$ K. In this temperature region, there are small systematic differences, similar to those noted earlier for CH$_3$D[10] and CH$_2$D$_2$,[11] which lie outside the expected error limits. The third set of results[18] is not plotted in Fig. 1 because it was only obtained for $T > 2.5$ K, but it has been shown[19] to be consistent with Colwell's data. Smoothed results (extrapolated to infinite sample size) for the present measurements of the heat capacity of CHD$_3$ are given in Table III.
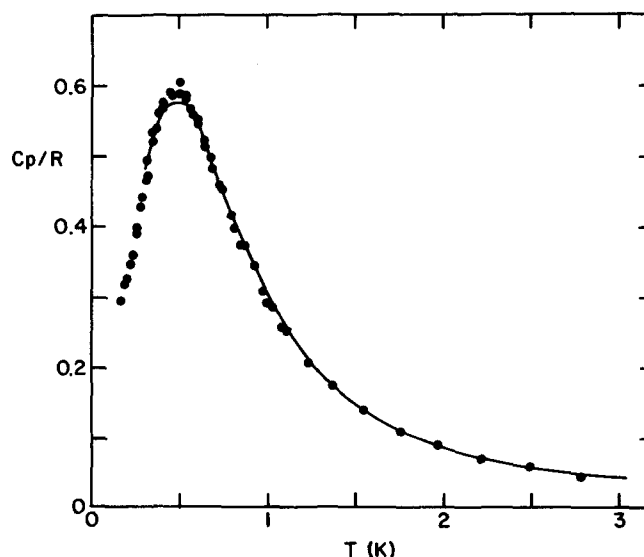

FIG. 1. The heat capacity of CHD$_3$ as a function of temperature: ● -present work; — -Colwell,[19] corrected and smoothed.

TABLE III. Smoothed values of the
heat capacity of pure CHD_3.

$T(K)$	C_p/R
0.14	0.242
0.16	0.276
0.18	0.301
0.20	0.323
0.22	0.343
0.24	0.367
0.26	0.392
0.28	0.420
0.30	0.448
0.35	0.512
0.40	0.561
0.45	0.579
0.50	0.582
0.60	0.535
0.70	0.469
0.80	0.400
0.90	0.339
1.00	0.288
1.50	0.141
2.00	0.081
2.50	0.055
3.00	0.041

Because of the compressed scale of Fig. 1, it is per-
haps not obvious that the Schottky anomaly in CHD_3 con-
tains some "structure." We will return to that later.

IV. DISCUSSION

A. The entropy of CHD_3

The entropy of CHD_3 gas at $T = 89.96$ K and $P = 0.1055$
atm, calculated from molecular properties and including
the contribution of the proton and deuteron spins, is[18]

$$S/R = 26.24 \pm 0.03 . \tag{5}$$

If, from this, we subtract entropy changes due to con-
densation, cooling, solidification, etc. for which ap-
propriate data are available here and elsewhere,[21,22]
we obtain the entropy of the solid as a function of tem-
perature as depicted in Fig. 2. It is useful to estimate
the residual entropy at $T = 0$ K by extrapolation from two
regions:

(i) $T \geq 8$ K, which neglects the contribution from the
Schottky anomaly

$$S_0/R = 5.37 \pm 0.10 ; \tag{6}$$

(ii) $T \leq 0.15$ K, which is from the lowest temperature
reached in the present experiments

$$S_0/R = 4.23 \pm 0.10 . \tag{7}$$

Result (6) corresponds exactly with $\ln 216$, which is the
entropy to be expected for the nuclear spin contribution
plus a contribution for random orientation of the C–H
bond in CHD_3:

$$S_0/R = \ln 3^3 \times 2 \times 4 = \ln 216 = 5.37 . \tag{8}$$

The interpretation, therefore, is that, down to $T \sim 8$ K,
the high temperature composition of nuclear spin sym-
metry species is maintained and no ordering of the

orientations of the C–H bonds has occurred.

If complete ordering were to occur without conver-
sion between nuclear spin symmetry species, the re-
sidual entropy to be expected is

$$S_0/R = \ln 54 = 3.99 , \tag{9}$$

which is less than result (7). This should now be com-
pared with the findings for CH_3D[10] and CH_2D_2.[11]

B. Entropy results for CH_3D and CH_2D_2

In the example of CH_3D, the residual entropy, ob-
tained by extrapolation from the lowest experimental
temperature, was less than that corresponding to com-
plete orientational ordering of the C–D bonds but greater
than the entropies for complete ordering plus complete
conversion to the A nuclear spin symmetry species.
Independent neutron cross section[10] and NMR[23] experi-
ments showed that conversion occurred in CH_3D in the
region $T < 10$ K and it was assumed[10] that it was essen-
tially complete at the lowest temperature reached in
the calorimetric experiments. Thus, it was deduced
that the entropy "shortage" was caused by incomplete
ordering.

For CH_2D_2, by contrast, neutron cross section mea-
surements yielded an ambiguous result regarding con-
version.[11] However, the complete absence of signifi-
cant thermal relaxation in the calorimetric experiments
led to the conclusion that conversion did not occur in
this methane. This was consistent with the determina-
tion that the entropy removed in the region $T < 8$ K was
less than that required for full orientational ordering of
the C–H and C–D bonds, viz., $\Delta S/R = \ln 6$. Result (7)
for CHD_3 can be expressed in similar terms; the de-
crease in entropy in the region $T < 8$ K is less than that
for full ordering: $\Delta S/R = \ln 4$.

C. Molecular field symmetry and possible tunneling levels for CHD_3

We now want to consider the residual entropy of CHD_3
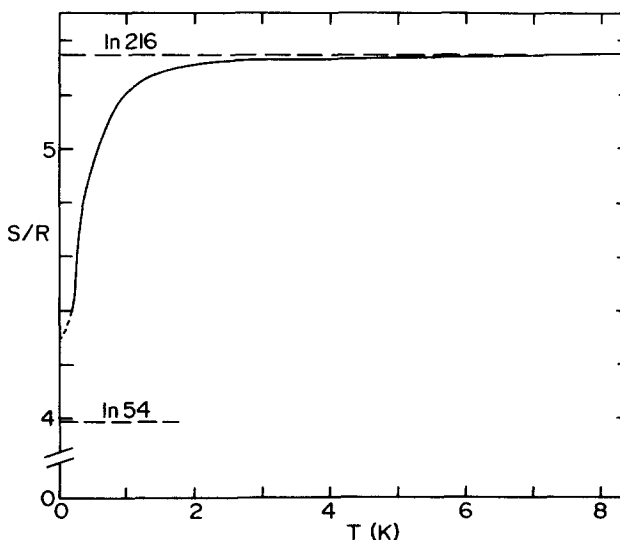in relation to the tunneling states which the molecules

FIG. 2. The entropy of CHD_3, including the contribution of
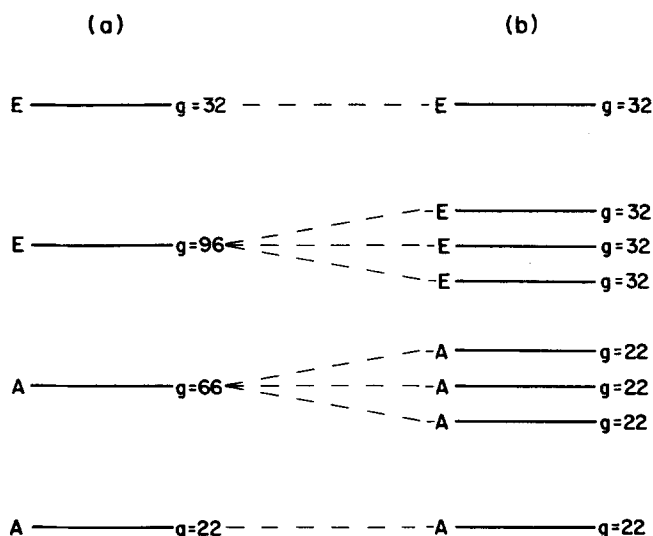nuclear spins, as a function of temperature.

(a)   (b)

E ————————— g = 32 — — — — — — —E ——————————— g = 32

                                                  — —E ——————————— g = 32
E ——————————g = 96 ≤ ≤ ≤ — — — —E ——————————— g = 32
                                                  — —E ——————————— g = 32

                                                  — —A ——————————— g = 22
A ——————————g = 66 ≤ ≤ ≤ — — — —A ——————————— g = 22
                                                  — —A ——————————— g = 22

A ——————————g = 22 — — — — — — —A ——————————— g = 22

FIG. 3. Schematic ground state manifold for CHD_3 molecules in two types of molecular fields: (a) tetrahedral, (b) asymmetric. A and E designate the two nuclear spin symmetry species and g = total degeneracy.

can occupy as determined by the symmetry of lattice sites in phase III. The premise is that the rotational motion of the molecules is hindered and that, at the low experimental temperatures, the molecules reorient by quantum mechanical tunneling. Some calculations for crystalline methane, based upon group theory, were made[24] some years ago and have been used subsequently in attempts to deduce energy levels for the isotopic methanes.[10,11,18,19,25] Figure 3 shows the ground state manifolds to be expected for CHD_3 molecules (a) in a tetrahedral crystal field and (b) in an asymmetric field. The values of g are the total degeneracies. The energy separation is not important here because our immediate concern is to compute the residual entropy in the limit $T \to 0$ K.

The high temperature equilibrium composition of nuclear spin symmetry species in CHD_3 is $A = 88/216$ and $E = 128/216$. If no conversion occurs, the residual entropy for molecules in a tetrahedral field is

$$\frac{S_0}{R} = \frac{88}{216}\ln22 + \frac{128}{216}\ln96$$
$$- \left(\frac{88}{216}\ln\frac{88}{216} + \frac{128}{216}\ln\frac{128}{216}\right) = 4.64 . \qquad (10)$$

For an asymmetric field, we obtain

$$\frac{S_0}{R} = \frac{88}{216}\ln22 + \frac{128}{216}\ln32$$
$$- \left(\frac{88}{216}\ln\frac{88}{216} + \frac{128}{216}\ln\frac{128}{216}\right) = 3.99 . \qquad (11)$$

Neither of these possibilities agrees with result (7) within its estimated uncertainty. We therefore conclude that phase III cannot be a structure which has all of the molecules on sites of the same molecular field symmetry.[26] That agrees with the conclusion reached[10,11] from analyses of results for CH_3D and CH_2D_2. In those examples, moreover, an attempt was made to invoke a

two sublattice structure for phase III, but this led to serious inconsistencies in the correlation of splittings of tunneling states with the possible molecular fields at the two types of sites. In a theoretical study of the structure of phase III,[12] it was also shown that a two sublattice model had limitations. We shall therefore investigate the extent to which a three sublattice model can be made to reproduce the experimental observations for all of the partially deuterated methanes.

D. Models for phase III

The information from experiment to be fitted by a model consists of (i) the residual entropy; (ii) the heat capacity as a function of temperature; and (iii) conversion in CH_3D but not in CHD_3 or CH_2D_2. In addition, of course, the tunneling levels that are derived should be consistent with the strengths of the supposed molecular fields at the lattice sites. It was in this respect that the two sublattice model was unsatisfactory[10,11] when applied to the examples of CH_3D and CH_2D_2. Three models will be discussed.

1. Model 1

This is the model determined theoretically by Maki et al.[12] as the most probable of several possibilities derived from a study of branching relationships. It has the tetragonal space group $P4_2/mbc$ with 16 molecules in the cubic unit cell. They are distributed as follows: four molecules on sites of S_4 symmetry, eight molecules on sites of C_s symmetry, four molecules on sites of D_2 symmetry. The molecular fields are presumed to be stronger at the S_4 and C_s sites than at the D_2 sites and to be of tetrahedral symmetry. With the assumption that conversion goes to completion in CH_3D but does not occur in CH_2D_2 or CHD_3, we obtain the residual entropies given in the first column of Table IV. They differ from the experimental estimates by more than the probable experimental error.

2. Model 2

A modification of the theoretical model produces better agreement with experiment. We preserve the assumption that the molecules on sites S_4 and C_s experience the stronger molecular fields but suppose that the symmetry of their fields is less than tetrahedral. Conversion is assumed to occur in CH_3D only on C_s and D_2 sites and not at all in CH_2D_2 and CHD_3. The corresponding residual entropies (second column of Table IV) now agree well with experiment.

3. Model 3

An even better model can be evolved by looking more closely at the results for CH_3D, and in particular at the

TABLE IV. The residual entropy S_0/R for three models of phase III.

	Model 1	Model 2	Model 3	Experiment
CH_3D	2.48	2.66	2.64	2.63 ± 0.10
CH_2D_2	4.22	3.74	3.79	3.84 ± 0.10
CHD_3	4.64	4.15	4.24	4.23 ± 0.10

TABLE V. Specifications for model 3 of phase III.

	Sites		
	Type 1	Type 2	Type 3
Molecular field symmetry	Tetrahedral	Tetrahedral	< Tetrahedral
Mole fraction	1/8	1/4	5/8
Conversion			
CH_3D	No	Yes	Yes
CH_2D_2	No	No	No
CHD_3	No	No	No

extent of conversion. Group theory[24] has shown that, in CH_3D, the degeneracy of the lowest A state is invariant to the molecular field symmetry ($g = 12$), while the lowest E state degeneracy will depend on the molecular field symmetry ($g = 36$ for tetrahedral, $g = 12$ for less than tetrahedral symmetry). The residual entropy of CH_3D[10] indicated that phase III does not show both complete ordering and complete conversion; the degeneracies of the lowest A and E states indicate that this additional entropy must be associated with the E species. Of course, in order for the E species to contribute at $T = 0$, conversion cannot be complete in CH_3D.

There are two possible ways to associate the residual entropy with the E species for CH_3D: The sublattice on which conversion does not take place could have a molecular field of tetrahedral symmetry or one of less than tetrahedral symmetry. To be consistent with the observed residual entropy for CH_3D, these symmetries would lead, respectively, to 1/8 and 1/4 of the molecules retaining their high temperature spin species composition.

The second possibility (i.e., 1/4 of the molecules) leads to model 2 discussed above. It, however, is not completely consistent with the results of measurements of total neutron cross sections for CH_3D.[10] While the cross section measurements were only carried down to $T \sim 0.75$ K, an extrapolation of the quantity $\langle I(I+1) \rangle$, where I is the total proton spin, as a function of temperature to $T = 0$ indicates that more than 3/4 of the CH_3D must convert.

The other possibility, that 1/8 of the CH_3D molecules are at sites of tetrahedral symmetry and do not undergo nuclear spin species conversion, is more consistent

with the neutron cross section measurements. Furthermore, to account for the observed entropy for CH_2D_2, it is necessary for the remaining 7/8 of the molecules to be split in the ratio 2 : 5 between molecular fields of tetrahedral and less than tetrahedral symmetries. This model gives the residual entropies in the third column of Table IV; they reproduce adequately those of CH_3D and CH_2D_2, and convincingly predict that for CHD_3. Model 3 is summarized in Table V.

Both models 2 and 3 satisfy the requirements of the residual entropies, and their three sublattice structures are consistent with results of recent spectroscopic experiments.[13,14] Also, the proportions of the different sublattices are sensible in relation to the structure of phase II, the connection to which has been emphasized by Maki et al.[12] However, to obtain an estimate of the tunneling states in CHD_3, we shall only use model 3.

E. Tunneling states

A preliminary analysis of the heat capacity data in the region $T < 0.5$ K indicated a ground state manifold of two groups of levels roughly in the proportions 2/3, which is close to the proportions $88/128 = 0.69$ of the A and E nuclear spin symmetry species in CHD_3. This was taken to confirm that conversion did not occur in this methane. It also indicated that the energy states must be rather similar for the different types of sites. As a consequence, the following simplifying assumptions could be made in deriving an estimate of the array of energy states for CHD_3:

(i) the two types of tetrahedral sites have the same tunnel splittings;

(ii) the molecular field at the nontetrahedral sites produces an additional splitting for the E species but not for the A species.

The model array is shown in Fig. 4 where the values given for g are total degeneracies. Since group theoretical arguments[19,25] indicate that the energy splitting for E molecules should be half that for A molecules, the derivation of the energy states can be reduced to a two parameter problem by taking $a = c = 2b = 2e$. The heat capacity data were fitted by linear least squares and the values $a = 1.55$ K and $d = 0.29$ K found for the two free parameters. The quality of the fit is displayed in Fig. 5. It is well within experimental error over the entire temperature range.
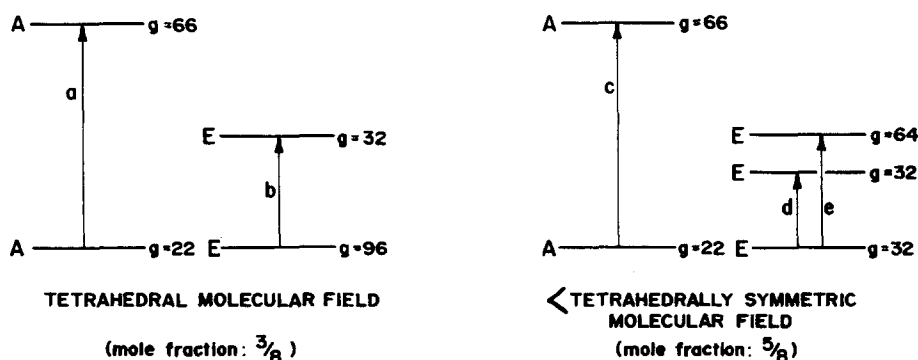

FIG. 4. Model of the ground state manifold of tunneling states in CHD_3. The energy parameters are related by $a = c = 2b = 2e$ (see text).
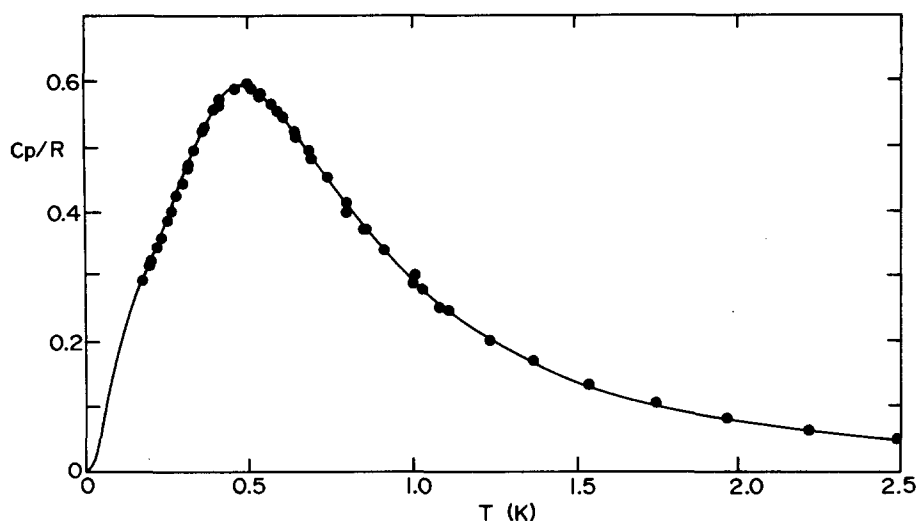
FIG. 5. The heat capacity of CHD_3 as a function of temperature: ●-experimental points; — -calculated from model displayed in Fig. 4 with $a = 1.55$ K and $d = 0.29$ K.

In his earlier work on the partially deuterated methanes, Colwell[19] sought to fit experimental heat capacities with models that assumed either tetrahedral or lower than tetrahedral symmetry. At the time, it was not suspected that phase III would have such a complicated sublattice structure. It is interesting that the array deduced in the present study is very similar to a combination of two arrays which Colwell considered (see Fig. 13 of Ref. 19).

In principle, the general model evolved here could be used to make estimates of the ground state manifolds of the tunneling states in CH_3D and CH_2D_2. The adoption of the ideas developed with the example of CHD_3 would undoubtedly remove the logical inconsistencies that resulted in the earlier attempts[10,11] to use a two sublattice model to derive the energies of the tunneling states. We have not pursued that because we believe it will now be more valuable to determine the positions of some of the energy states directly by, for example, inelastic neutron scattering.

V. SUMMARY

Heat capacity measurements and entropy calculations for solid CHD_3 have been used to obtain estimates of tunneling states that describe reorientation of the molecules on the lattice sites. The minimum complexity that is acceptable for phase III of solid methane is a three sublattice structure. This conclusion is in agreement with one drawn from a theoretical investigation[12] and recent spectroscopic evidence.[13,14] However, the experimental results for CHD_3, together with earlier ones obtained for CH_3D[10] and CH_2D_2,[11] permit significant refinement of the theoretical model to be made.

No evidence has been found for conversion between nuclear spin symmetry species of CHD_3. In this respect, CHD_3 behaves like CH_2D_2 but not like CH_3D, for which it is deduced that conversion occurs on two of the three sublattices which comprise 7/8 of the molecules.

All three of the partially deuterated methanes are quantum disordered[27] at the lowest temperatures reached in the calorimetric experiments ($T \sim 0.15$ K). This deduction has structural implications which will need to

be pursued in the determination of a space group for phase III.

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