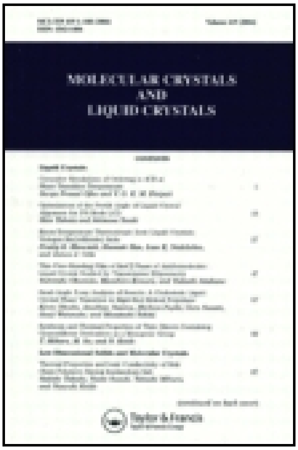

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# Qualitative Classification of Tetrahedral Molecular Crystals

Takako Shinoda [a]
[a] National chemical Laboratory for Industry, Tsukuba Research Center, Yatabe, Ibaraki, 305, Japan

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# Qualitative Classification of Tetrahedral Molecular Crystals

TAKAKO SHINODA

***National Chemical Laboratory for Industry, Tsukuba Research Center, Yatabe, Ibaraki 305, Japan***

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From the point of view of molecular interactions, an attempt has been made to classify tetrahedral molecular crystals qualitatively by using experimental data of crystal structures, the Debye characteristic temperature at 0 K, $\theta_D(0)$, assuming 6N degrees of vibrational freedom, and the transition or melting temperatures.

## INTRODUCTION

Non-polar tetrahedral molecules $XY_4$ ($X = C, Si, Ge$, and $Y = H, D, CH_3, F, Cl, Br$) are grouped into two classes: one which undergoes phase transition in the solid state, and the other which does not. In the previous papers, we studied some of the tetrahedral molecules by treating $SiF_4$ as a standard substance and by applying the model of the interaction potential (for the pair of molecules) which is made up of the following terms:

1) a spherical interaction potential of the Lennard-Jones form (6–12),

2) an anisotropic Lennard-Jones potential between nonbonded atoms of molecules, and

3) a term due to the electrostatic octopole—octopole interaction between neighboring molecules.

The Debye characteristic temperature at 0 K, assuming 6N degrees of vibrational freedom (where N is Avogadro's number), was estimated from the observed heat capacity data of $XY_4$. In the present paper, we attempted to classify $XY_4$ molecules qualitatively into four groups from the point of view of molecular interactions.

## METHOD AND RESULTS

There is no calculation of the lattice vibrations of $XY_4$ by using a realistic molecular potential and experimental crystal structure. The Debye characteristic temperature at 0 K, $\theta_D(0)$, is one of the experimental data which can be correlated with molecular interactions. Since it is difficult to calculate the lattice vibrations of $XY_4$, even to obtain the thermodynamic properties of all tetrahedral molecular crystals which are treated in the present paper, we attempted to apply the Lindemann's law parameters for convenience' sake. The Lindemann's law of melting or rotational melting transition is written as follows:

$$T_m = Dm\theta_D^2a^2 \qquad (1)^1$$

where $T_m$ is melting temperature, $D$ a constant, $m$ the molecular weight, $\theta_D$ the Debye temperature, and $a$ the intermolecular spacing. And

$$T_r = D'I\theta_E^2\psi_0^2 \qquad (2)^2$$

where $T_r$ is the transition temperature, $D'$ a constant, $I$ the average moment of inertia of the molecule, $\theta_E$ the Einstein temperature, and $\psi_0$ the angle between the potential minima. It appears best to use $\theta_D(0)$ as the value of $\theta_D$ and $\theta_E$ estimated from the results of the calculation of lattice vibration of molecular crystals.[3] The values of $D$ and $D'\psi_0^2$ for $XY_4$ which are estimated by relations (1) and (2) are summarized in Table I together with experimental data used in the estimation.

Group-I is $SiF_4$ which is a standard substance in tetrahedral molecular crystals. The crystal structure is a b.c.c. lattice, and the molecular orientation in the crystal minimizes the potential energy in terms of electrostatic octopole—octopole interactions between neighboring molecules. The anisotropic interaction potential between nonbonded atoms of molecules is not so important.[4] $D$ and $D'\psi_0^2$ were estimated as $0.314 \times 10^{35}$ and $5.83 \times 10^{35}$, respectively.

Group-II consists of tetrahedral molecular crystals which transform from a monoclinic lattice to a cubic or tetragonal one with increasing temperature. $CF_4$, $C(CH_3)_4$, $CCl_4$ and $CBr_4$ are in this group. The lattice parameters of the monoclinic unit cell are listed in Table II. The ratio of a:b:c and the angle of monoclinicity can approximate $2\sqrt{2}:\sqrt{2}:2\sqrt{2}$ and 120°, respectively, excepting $C(CH_3)_4$ where crystal structure has not been studied unambiguously in the low temperature phase. The number of molecules per unit cell is 4 or 32 $(= 4 \times 2^3)$.

A half of monoclinic unit cell which has the following parameters: $a = c = 2\sqrt{2}$, $b = \sqrt{2}$, $\beta = 120°$, in which four molecules are centered at (0, 0, 0), $(\frac{1}{2}, \frac{1}{2}, 0)$, $(0, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, is equal to a body-centered tetragonal lattice which has $a = b = \sqrt{2}$, $c = 2\sqrt{2}\sin(60°) = \sqrt{6}$ in which two molecules are

## TABLE I

Estimated $D, D'\psi_0^2$ and the data used in the estimation for $XY_4$ and related substances

| | $T_r$ (K) | $T_m$ (K) | $\theta_D$ (O) (K) | $I \times 10^{40}$ (g cm$^2$) | $a$ (A) | $D \times 10^{-35}$ (erg$^{-1}$K$^{-1}$sec$^{-2}$) | $D'\psi_0^2 \times 10^{-35}$ (erg$^{-1}$K$^{-1}$sec$^{-2}$) |
|---|---|---|---|---|---|---|---|
| $SiF_4$ | — | 186.35[a] | 125.0 ± 0.4[b] | 204.7 | 4.685 | 0.314 | 5.83 |
| $CF_4$ | 76.221[c] | 89.529[c] | 108.7[c] | 146.7 | 4.674 | 0.237 | 4.40 |
| $C(CH_3)_4$ | 140.498[d] | 256.756[d] | 125.9[d] | 186.2 | 6.102 | 0.363 | 4.76 |
| $CCl_4$ | 225.7 (II → Ib)[e] | 246.00 (Ia)[e] | 122.7[e] | 489.1 | 5.897 | 0.184 (Ia) | 3.07 (II → Ib) |
| | | 250.53 (Ib)[e] | 122.7[e] | 489.1 | 5.802 | 0.194 (Ib) | — |
| $CBr_4$ | 320.1[f] | 363.3[f] | — | 1293.5 | 6.24 | — | — |
| $CH_4$ | 20.49 (II → I)[g] | 90.675[g] | 110.7[g] | 5.3402[h] | 4.16 | 1.61 | 31.3 (II → I) |
| | 8 (hidden tr.)[i] | — | 110.7 | 5.3402 | — | — | 12.2 (hidden tr.) |
| $CD_4$ | 22.1 (III → II)[j] | — | 170.3[j] | 10.6390[k] | — | — | 7.16 (III → II) |
| | 27.0 (II → I)[j] | 89.784[j] | 170.3 | 10.6390 | 4.13 | 0.54 | 8.75 (II → I) |
| α-$Si(CH_3)_4$ | — | 165.920[l] | — | — | — | — | — |
| β-$Si(CH_3)_4$ | — | 170.983[l] | 136.8 ± 2.0[l] | 272.0 | — | — | 3.36 |
| γ-$Si(CH_3)_4$ | — | 174.074[l] | 147 ± 2[l] | 272.0 | — | — | 2.96 |
| Ar | — | 83.8[m] | 93.3 ± 0.6[m] | — | 3.752 | 1.03 | — |
| Kr | — | 115.776[m] | 71.7 ± 0.7[m] | — | 3.992 | 1.02 | — |
| CO | 61.570 | 68.154 | 124.5 | 14.49 | 4.14 | 0.55 | 27.4 (α → β) |
| | 18 (hidden tr.)[n] | — | 124.5 | 14.49 | — | — | 8.01 (hidden tr.) |

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TABLE II

Lattice parameters of group-II $XY_4$ molecules in the low temperature phase

| Material | $a$(A) | $b$(A) | $c$(A) | $\beta$(°) | Ref. |
|---|---|---|---|---|---|
| $CF_4$ | $2a = 5.964 \times 2\sqrt{2}$<br>$= (6.887 \times \sqrt{6})$ | $2b = 6.110 \times \sqrt{2}$ | $2c = 5.918 \times 2\sqrt{2}$<br>$= (6.833 \times \sqrt{6}$ | 119.40 | 8 |
| $C(CH_3)_4$ | Hexagonal ($a$ = 14.3 A, $c$ = 8.84 A) | | | | 6 |
| $CCl_4$ | $20.3 = 7.18 \times 2\sqrt{2}$<br>$= (8.29 \times \sqrt{6})$ | $11.6 = 8.20 \times \sqrt{2}$ | $19.9 = 7.04 \times 2\sqrt{2}$<br>$= (8.12 \times \sqrt{6})$ | 111 | 9 |
| $CBr_4$ | $21.43 = 7.577 \times 2\sqrt{2}$<br>$= (8.749 \times \sqrt{6})$ | $12.12 = 8.570 \times \sqrt{2}$ | $21.02 = 7.432 \times 2\sqrt{2}$<br>$= (8.581 \times \sqrt{6})$ | 110.88 | 7 |

centered at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and (0, 0, 0) or $(0, \frac{1}{2}, 0)$ per unit cell. That is to say, the crystal structure of group-II $XY_4$ molecules in the low temperature phase is nothing but a body-centered lattice which is a strained b.c.c. This strain seems to be caused by an anisotropic L-J potential between nonbonded atoms of molecules, estimated from the results of the calculation of the intermolecular potential for $CF_4$.[5]

The hexagonal lattice of $C(CH_3)_4$ observed at −155°C by Rudman and Post[6] may be also similar to a body-centred lattice.

The crystals of group-II are face centered cubic lattices in the high temperature phase. A monoclinic unit cell can be converted into a cubic cell.[7] The numerals in parenthesis given in Table II indicate that the calculated lattice constant of the pseudocubic cell from the lattice parameters of monoclinic cell is close to its f.c.c. lattice constant (8.34 A; $CCl_4$, 8.82 A; $CBr_4$) in the high temperature phase. The positions of the center of the molecules are equal to those in the crystal structure of rare gas solids. Thus, the transition is an orientational order-disorder one.

The mean value of $D$ for group-II is about $0.3 \times 10^{35}$ as shown in Table I and is nearly equal to the D-value obtained for $SiF_4$, although $D$ for $CBr_4$ was not estimated since the $\theta_D$ value is unknown. On the other hand, the mean value of $D'\psi_0^2$ for group-II is about $4.5 \times 10^{35}$ excepting $CCl_4$, and is smaller than that for $SiF_4$. If we put $\psi_0 = \pi/2$, $D'$ is estimated as $1.8 \times 10^{35}$.

Group-III consists of tetrahedral molecular crystals which undergo orientational disordering transition, in which the relevant intermolecular interaction is essentially an effective octopole-octopole interaction. $CH_4$, $CD_4$, $SiH_4$ and $GeH_4$ may be in this group. The transitions of $CH_4$ and $CD_4$ have successfully been studied on the basis of the James-Keenan model[10] as the first approximation, and then developed by Yamamoto and his group.

The molecular orientation, i.e. the positions of hydrogen atoms in each phase have not been evident experimentally for any molecular crystal of group-III. Therefore, we have not studied the intermolecular potential for this group. It has been reported by some authors that the structure of the center of the molecules in the lowest temperature phase is body-centred tetragonal for $CD_4$[11] and $SiH_4$.[12] One may say that the crystal structure of group-III in the lowest temperature phase is a body-centred lattice as well as of groups I and II.

The D-value is $1.61 \times 10^{35}$ for $CH_4$, which is close to that for rare gas solid, and is $0.54 \times 10^{35}$ for $CD_4$, which is close to that for the diatomic molecule (CO) as shown in Table I. $D'\psi_0^2$ is about $30 \times 10^{35}$ for $CH_4$ and $7 - 9 \times 10^{35}$ for $CD_4$. The values of $D$ and $D'\psi_0^2$ for group-III are different from those for groups I and II. These value of $D$ and $D'\psi_0^2$ suggests the configuration of molecular motions in the crystal below the transition or melting point by comparing with the values for rare gas solid and diatomic molecule that its transitions are interpreted in terms of multipole interaction as the first approximation. For example, $CH_4$ melts in a configuration of pseudo-free rotation and $CD_4$ just below melting is close to the $\beta$-CO solid. The transition of $CH_4$ is one to free rotation (or hindered rotation) as well as CO (from $\alpha$ to $\beta$). On the other hand, the transition of $CD_4$ is one to some equilibrium orientation which is close to the hidden transition of CO.

Group-IV consists of tetrahedral molecular crystals which do not undergo phase transition below the melting point as the temperature is increased. $Si(CH_3)_4$, $Ge(CH_3)_4$, $SiCl_4$, $GeCl_4$, $SiBr_4$ and $GeBr_4$ may be in this group. The crystal structures and thermodynamic properties of tetrahedral molecules of group-IV have been little studied. There are three crystalline forms designated by $\alpha$, $\beta$ and $\gamma$ in solid-Si $(CH_3)_4$. The transitions $\alpha$-to-$\beta$-to-$\gamma$ seem to be irreversible. It has been reported that there are stable and metastable states in solid-$GeCl_4$.[13] The polymorphism in the solid is probably related to some potential minima of rotation with a small difference in energy.

For group-IV the D-value cannot be assumed since the molecular distance in the solid is unknown, and the $D'\psi_0^2$-value may be $3 \times 10^{35}$, from the results of the estimation for $Si(CH_3)_4$ as shown in Table I.

## DISCUSSION

Although the Lindemann's law parameters have no important physical meaning, these may be useful for characterizing each group of $XY_4$ qualitatively.

Assuming $\theta_D(0) = 75$ K which gives the mean value of $D$ $(0.3 \times 10^{35})$ for $CBr_4$, $D'\psi_0^2$ is estimated as $4.4 \times 10^{35}$ and equal to the mean value of $D'\psi_0^2$ for group-II.

The anomalous small values of $D$ and $D'\psi_0^2$ for $CCl_4$ may be accounted for by the experimental result that liquid $CCl_4$ has a long-range correlation[14] and some experimental errors. In Figure 1 the heat capacities of $CF_4$, $C(CH_3)_4$ and $CCl_4$ in the range $T < 10$ K are plotted in the form of $C_p/T^3$ against $T^2$. Here we find that the shape of the curves for $CF_4$ and $C(CH_3)_4$ are similar to each other and are different from that for $CCl_4$. If we estimate the $\theta_D(0)$ for $CCl_4$

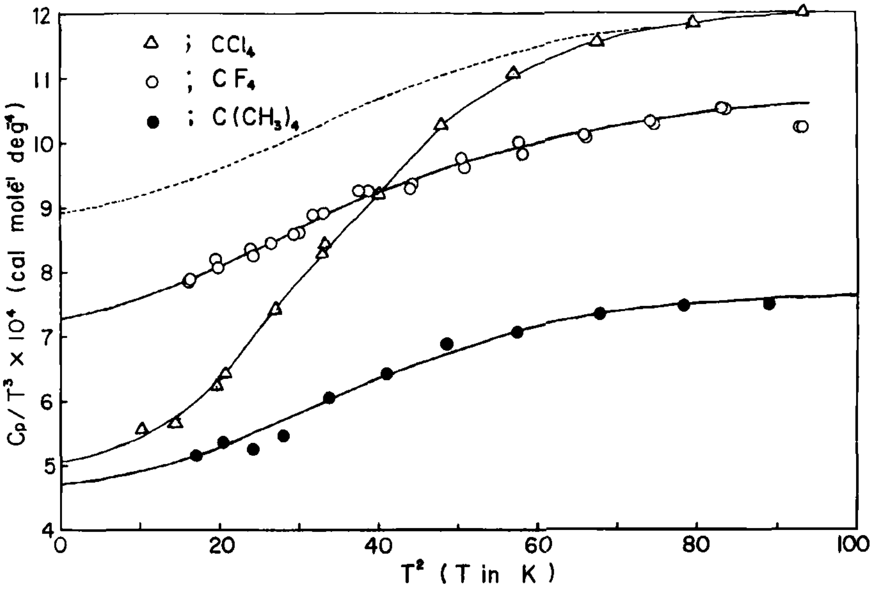

FIGURE 1 Plots of $C_p/T^3$ against $T^2$ for tetrahedral molecular crystals of group-II (1 cal = 4.1840 J).

assuming the dashed curve as shown in Figure 1 which is similar to those for $CF_4$ and $C(CH_3)_4$, the $\theta_D(0)$ value of 101.6 K is obtained, which gives $D(\mathrm{Ia}) = 0.27 \times 10^{35}$, $D(\mathrm{Ib}) = 0.28 \times 10^{35}$ and $D'\psi_0^2 = 4.47 \times 10^{35}$.

Using $\theta_D = 120.7$ K at 11.35 K, which is the lowest temperature among the measurements of heat capacity[15] for $SiH_4$, $D$ and $D'\psi_0^2$ are estimated as $0.53 \times 10^{35}$ and $44.6 \times 10^{35}$ for $SiH_4$, respectively. Here the experimental data ($T_r = 63.45$ K,[15] $T_m = 88.48$ K,[15] $I = 9.77 \times 10^{-40}$ g cm$^2$ [16] and a = 4.615 A[13]) were used. Guessing from this result, it seems that $SiH_4$ just below the melting is in close configuration to $CD_4$ and the transition is close to free rotation or hindered rotation. The transition temperatures of $GeH_4$ are 62.9 K, 73.20 K and 76.55 K,[17] and the estimated values of $D'\psi_0^2$ are to be larger than $30 \times 10^{35}$, using $I = 10.42 \times 10^{-40}$ g cm$^2$ [18] and $\theta_D = 95.9$ K at 12.00 K which is the lowest temperature among the measurements of heat capacity.[17] Therefore, the transitions of $GeH_4$ may be to free or hindered rotation as well as $CH_4$.

If we estimate the $\theta_D(0)$ for some molecules of group-IV, which gives the $D'\psi_0^2$ — value of $3 \times 10^{35}$, we can guess that the values of $\theta_D(0)$ are 144 K, 103 K, 105 K and 75 K for $Ge(CH_3)_4$ ($T_m = 184.368$ K,[19] $I = 296.6 \times 10^{-40}$ g cm$^2$), $SiCl_4$($T_m = 204.3$ K,[20] $I = 640.6 \times 10^{-40}$ g cm$^2$), $GeCl_4$($T_m = 223.7$ K,[21] $I = 679.2 \times 10^{-40}$ g cm$^2$) and $SiBr_4$($T_m = 278.4$ K, $I = 1628 \times 10^{-40}$ g cm$^2$), respectively.

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