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# On the Crystal Structure of Methane in Phase II

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It is well known that there are two kinds of second-order phase transitions in solid methane, at 4.20°K and at 8°K. The most likely explanation of these transitions is that these are changes in the molecular orientation[1], but their exact mechanism and the structure of the each phase are still ambiguous.

X-Ray diffraction studies[2-4] show that the carbon atoms occupy *fcc* positions over the whole temperature range from 4.2 to 80°K. For the *fcc* carbon lattice, there are several possible structures, differing in the relative orientations of their molecules.

The IR and Raman spectra[5,6] of Phase II(20.4> $T$°K>8) were explained by postulating sites of either $C_{2v}$ or $D_2$ structures.

Kimel *et al.*[7] have calculated the cohesive energy of crystalline methane for various possible structures using a potential function consisting of repulsive and attractive interactions between non-bonded atoms. They found that the tetragonal structures of the $D_{3d}$ symmetry have the best paking.

In a previous work,[8] we found, for the $C_2H_2$ crystal, that the pair-potential calculation makes it possible to determine the space group when the crystal system and the lattice constants are already known.

In the present note, we will see, for the crystalline methane, that if the distance between the nearest two molecules is known, it is possible to determine not only the crystal system, but also the space group. This finding is very interesting, since the mechanism of

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4) W. Gissler and M. Stiller, *Naturwissenschaften*, **52**, 512 (1965).
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6) C. Chapados and A. Cabana, *Chem. Phys. Lett.*, **7**, 191 (1970).
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molecular condensation or crystallization can now be explained by means of pair-interaction potentials. All the computational work in this note were done at the Computer Center of Tohoku University using NEAC-2200-500 computer system.

## Intermolecular Potential

Assuming the spherical symmetry of the component atoms of the methane molecule, the following equation was used to calculate the pair-potential energy:

$$v(r) = \sum_j (a_j \exp(-b_j r_j)/r_j d_j - c_j/r_j^6), \qquad (1)$$

where the summation, $j$, is extended to all the interatomic pairs of the two molecules. The $a_j$, $b_j$, $c_j$, and $d_j$ parameters have been determined by several authors[9,10] so as to give the best agreement with the experimental results (see Table 1).

The relative orientation of the two interacting molecules is defined as is shown in Fig. 1.

Table 1. Set of parameters in Eq. (1)
set a: Ref. 9; set b: Ref. 10

| atom-atom | set | a×10⁻³ | b | c | d |
|---|---|---|---|---|---|
| C···C | a | 237.0 | 4.32 | 298.0 | 0.0 |
| | b | 408.0 | 0.0 | 373.0 | 12.0 |
| C···H | a | 31.4 | 4.20 | 121.0 | 0.0 |
| | b | 205.0 | 0.0 | 133.0 | 12·0 |
| H···H | a | 6.60 | 4.08 | 49.2 | 0.0 |
| | b | 4930.0 | 0.0 | 51.5 | 12.0 |

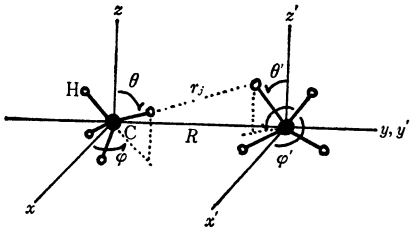


Fig. 1. The geometrical representation of two interacting methane molecules.

## Calculation and Results

Figs. 2 and 3 indicate the $v(r)$ when $\varphi'=270°$ and $\theta'=0°$. Among the $v(r)$ values for various $\theta'$ and $\varphi'$, those given in Figs. 2 and 3 have the deepest minimum. Since the methane molecule has a tetrahedral symmetry, there are twelve such minima about each methane molecule. Their centers of gravity form a face-centered cubic lattice. In each molecule three C–H bonds are placed nearly parallel to the $a$, $b$, and $c$ cubic axes, and the remaining one, parallel to the direction of the body diagonals (see Fig. 4). This structure belongs to the $T^4$-$P2_13$ space group and is just the one suggested by Nagamiya[11].

Recently Savoie *et al.*[12] have proposed the $T^4$-$P2_13$ space group for the structure of Phase II on the basis of the far infrared data. This is also consistent with our results.

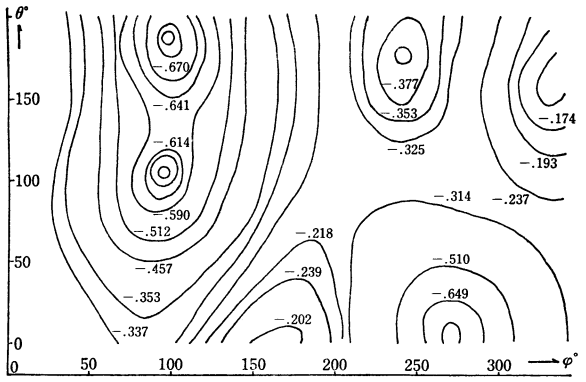


Fig. 2. $\theta$-$\varphi$ dependency of the pair potential using set b, in kcal/mol.

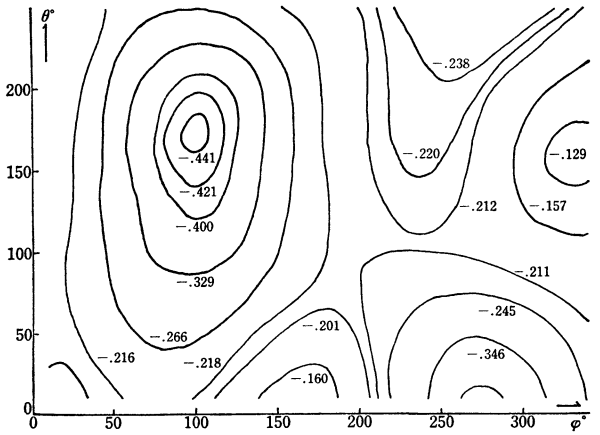


Fig. 3. $\theta$-$\varphi$ dependency of the pair potential using set a, in kcal/mol.

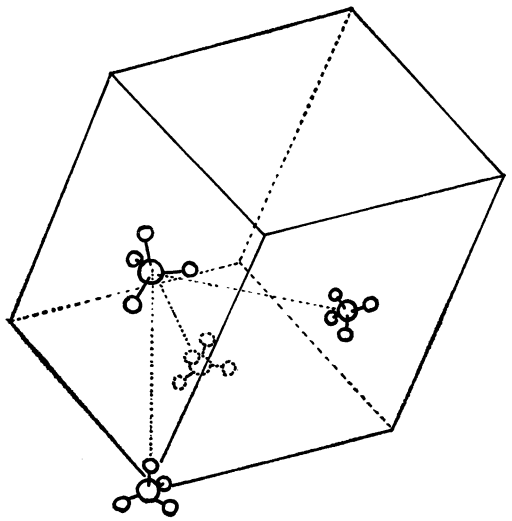

Fig. 4. The orientation of molecules that minimizes the pair potential when R=4.16 Å.

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10) N. G. Parsonage and R. C. Pemberton, *Trans. Faraday Soc.*, **63**, 311 (1967).
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The summation of $v(r)$ over the twelve nearest neighbours is 5.9 kcal/mol; this is roughly comparable with twice the sublimation energy of solid methane[13] at 0°K, 4.4 kcal/mol.

It may be suggested that the mechanism of the phase transition is a rotational one from the double minima in Fig. 2, but it is still ambiguous, for there are no such minima in Fig. 3. The validity of the parameters of Eq. (1) must be studied further.

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