NORMAL OSCILLATIONS OF THE T_d CLASS DIAMOND STRUCTURE

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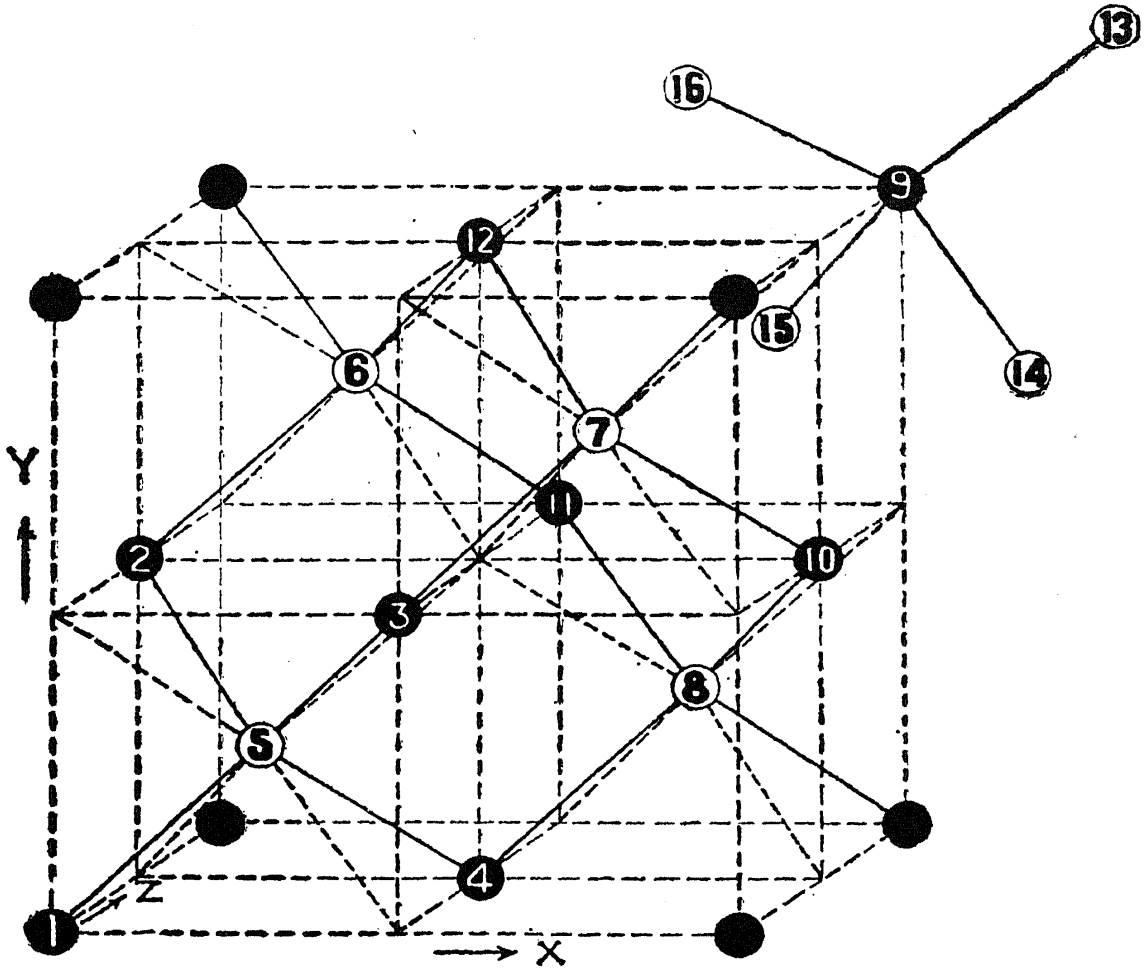
1. *Introduction*

In an earlier paper,[1] group theoretical methods have been used by the author for obtaining the normal oscillations of the O_h class diamond structure and the results appropriate to a repeating unit which has eight times the volume of the smallest unit cell were given. Such a repeating unit is formed by taking twice the primitive translation as the side of the cell along each direction instead of the primitive translation itself and contains 16 carbon atoms whereas the smallest one contains only 2.

It has been recently suggested by Raman[2] that the commoner type of diamond has only tetrahedral symmetry and should be placed under the T_d class. It is considered desirable to work out the normal oscillations of this structure also. In the present paper, results of applying group theoretical methods to such a structure are given. So that the results may be applicable to other tetrahedral crystals also (T_d class), a diamond arrangement with half its atoms different from the rest is assumed. Such an assumption automatically secures the absence of a centre of symmetry. The repeating unit is again formed by taking twice the primitive translation as the side of the cell along each direction instead of the primitive translation itself. Such a cell contains 8 atoms of type I and 8 atoms of type II whereas the smallest one contains only one of each.

2. *T_d Class Diamond Structure and its Symmetry Operations*

In Fig. 1 is shown a portion of this structure which is made up of two interpenetrating lattices. The dark circles denote type I atoms whereas the white circles denote the type II atoms. The smallest unit cell is a rhombohedron formed by the primitive translations 1,2; 1,3 and 1,4. Such a rhombohedron contains only two distinct atoms which are numbered 1 and 5. In such a case translations 1,2; 1,3 and 1,4 cannot be regarded as distinct from the identity operation and all the atoms numbered 2, 3, 4, 9, 10, 11 and



	E	32 c_3	6 c_2	12 σ	24 S_4	24 S_4	6 c_2	12 c_2	6 T	24 σ	32 c_3	12 σ	T	n_i
A_1 ..	1	1	1	1	1	1	1	1	1	1	1	1	1	0
A_2 ..	1	1	1	−1	−1	−1	1	1	1	−1	1	−1	1	0
E_1 ..	2	−1	2	0	0	0	2	2	2	0	−1	0	2	0
F_1 ..	3	0	−1	−1	1	1	−1	−1	3	−1	0	−1	3	0
F_2 ..	3	0	−1	1	−1	−1	−1	−1	3	1	0	1	3	2
F_3 ..	3	0	3	1	−1	1	−1	−1	−1	−1	0	1	3	1
F_4 ..	3	0	3	−1	1	−1	−1	−1	−1	1	0	−1	3	0
H_1 ..	6	0	−2	0	0	0	−2	2	−2	0	0	0	6	2
F_5 ..	3	0	−1	1	1	−1	3	−1	−1	−1	0	1	3	1
F_6 ..	3	0	−1	−1	−1	1	3	−1	−1	1	0	−1	3	0
K_1 ..	4	1	0	2	0	0	0	0	0	0	−1	−2	−4	2
K_2 ..	4	1	0	−2	0	0	0	0	0	0	−1	2	−4	0
M_1 ..	8	−1	0	0	0	0	0	0	0	0	1	0	−8	2
U_R ..	16	4	4	8	2	2	4	0	0	0	0	0	0	
$h_j x_j$ ..	48	0	−24	96	−48	−48	−24	0	0	0	0	0	0	

12 are equivalent to 1, whereas those numbered 6, 7, 8, 13, 14, 15 and 16 are equivalent to 5. The symmetry group will then consist of 24 elements only and may easily be dealt with.* The unit cell chosen in this paper is, however, a larger rhombohedron formed by the primitive translations which are twice 1,2; 1,3 and 1,4. Such a rhombohedron contains 16 distinct atoms which are numbered 1 to 16 in Fig. 1. Besides the 24 elements of the simple group, seven translations (1,2; 1,3; 1,4; 1,9; 1,10; 1,11; 1,12), which were hitherto identical with the identity element, have now to be regarded as distinct symmetry operations. These, along with the identity operation constitute a sub-group of order 8 and the total group of symmetry operations appropriate to this structure in which there are 16 non-equivalent points as shown in Fig. 1, will be formed by obtaining the product of the simple 24 elements with the above translational group consisting of 8 elements. The resulting group is of order 192. The elements of this group fall into 13 conjugate classes† and the appropriate character table is given here. The notation used is similar to that employed in the earlier papers of the author. The table shows that besides the translation, there are three threefold, two sixfold, two fourfold and two eightfold degenerate normal oscillations coming under various symmetry classes. Translation comes under the class F_2.

If all the last eight columns and the last eight rows are deleted, we get the character table containing only five conjugate classes and if the number of elements in each conjugate class is properly adjusted, we get results that are appropriate to the simple group of 24 elements which refers to the case where the smallest cubic cell containing 2 atoms only is regarded as the repeating unit.

3. Normal Modes and Normal Frequencies

Below is given one representative mode under each class. Those omitted may be written down from considerations of symmetry and taking into account the order of degeneracy in each case and the manner in which each normal co-ordinate transforms under the different symmetry operations. If the normal co-ordinates given below are read with reference to Fig. 1, it is easy to get a physical picture of each one of the modes.

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* Identity, eight trigonal axes, three digonal axes, six planes of reflection and six tetragonal rotation reflection axes constitute these 24 elements.

† Writing down all the 192 elements in the form of circular permutations and classifying them into conjugate classes is a very laborious process but follows the well-known methods of group theory. Details are not given here as they would occupy much space.

$$m_2(x_1+x_2+x_3+x_4+x_9+x_{10}+x_{11}+x_{12}) - m_1(x_5+x_6+x_7+x_8+x_{13}+x_{14}+x_{15}+x_{16}) \quad .. \quad F_2$$

$$(x_5+x_6)-(x_7+x_8)+(x_{13}+x_{14})-(x_{15}+x_{16}) \quad .. \quad .. \quad F_3$$

$$(x_1+x_2)-(x_3+x_4)+(x_9+x_{10})-(x_{11}+x_{12}) \quad .. \quad .. \quad F_5$$

$$\left.\begin{array}{l}(x_1-x_2+x_3-x_4)+(x_9-x_{10}+x_{11}-x_{12}) \quad .. \quad .. \quad ..\\ (y_5-y_6+y_7-y_8)+(y_{13}-y_{14}+y_{15}-y_{16}) \quad .. \quad .. \quad ..\end{array}\right] \quad H_1$$

$$\left.\begin{array}{l}(p_2+p_3+p_4+p_9)-(p_1+p_{10}+p_{11}+p_{12}) \quad .. \quad .. \quad ..\\ (p_6+p_7+p_8+p_{13})-(p_5+p_{14}+p_{15}+p_{16}) \quad .. \quad .. \quad ..\end{array}\right] \quad K_1$$

$$\left.\begin{array}{l}(x_1-z_1)+(x_2-z_2+x_3-z_3+x_4-z_4)+(x_9-z_9) \\ \quad -(x_{10}-z_{10}+x_{11}-z_{11}+x_{12}-z_{12}) \quad ..\\ (x_5-z_5)-(x_6-z_6+x_7-z_7+x_8-z_8)-(x_{13}-z_{13}) \\ \quad +(x_{14}-z_{14}+x_{15}-z_{15}+x_{16}-z_{16}) \quad .. \quad ..\end{array}\right] \quad M_1$$

p in K_1 stands for a displacement x, y, z. m_1 and m_2 are respectively the masses of the type I and the type II atoms. The frequencies of these modes can be evaluated in the usual manner. Below is given a statement which shows the frequency in each case and contains a description of the corresponding normal mode.* λ stands for $4\pi^2\nu^2$. μ is the reduced mass and $\frac{1}{\mu}=\frac{1}{m_1}+\frac{1}{m_2}$. K_1 is the force constant referring to any pair of atoms which constitute the nearest neighbours. K_3' and K_3'' are the force constants referring respectively to the nearest pair of type I atoms and of type II atoms. K_2' and K_2'' respectively represent the forces called into play when the angle between any two valence bonds which meet at the type I and the type II atom varies. p stands for the distance between a pair of nearest neighbours and is the same as the length of the valence bond.

It may be noted that if m_1 and m_2 are both replaced by m, the mass of a carbon atom, K_2' and K_2'' are both replaced by K_2 and K_3' and K_3'' are both replaced by K_3, the structure reduces to that of O_h diamond as a centre of symmetry is automatically introduced. In such a case it is easily verified that the fequency of F_2 becomes identical with that of F_2 in O_h diamond.[1] The frequencies F_3 and F_5 become identical and they together correspond to the sixfold frequency H_1 of O_h diamond. The pair coming under H_1 pass over into the two coming separately under H_2 and H_4 in O_h diamond. Similarly, the pairs coming under K_1 and M_1 pass over respectively into those

* K and p occurring here have a different significance and are not to be confused with those occurring in the normal modes.

Mode		Degeneracy	λ
F_2 (1)	One interpenetrating lattice oscillating against the other	3	$\lambda_1=\frac{4K_1}{3\mu}+\frac{16(K_2'+K_2'')}{3p^2\mu}$
F_3 (1)	Consecutive planes parallel to the cube faces of any one lattice moving along the cubic axis normal thereto in opposite directions, while those belonging to the other lattice remain at rest	3	$\lambda_2=\frac{1}{m_2}\left[\frac{4K_1}{3}+8K_3''+\frac{16K_2''}{3p^2}+\frac{8K_2'}{p^2}\right]$
F_5 (1)	Do.	3	$\lambda_3=\frac{1}{m_1}\left[\frac{4K_1}{3}+8K_3'+\frac{16K_2'}{3p^2}+\frac{8K_2''}{p^2}\right]$
H_1 (2)	Consecutive planes parallel to the cube faces of any one lattice moving transverse to the cubic axis normal thereto in opposite directions while those of the second lattice do the same thing	6	$\lambda_4+\lambda_5=\frac{4K_1}{3\mu}+\frac{4K_3'}{m_1}+\frac{4K_3''}{m_2}+\frac{1}{3m_1p^2}\left[4K_2''+16K_2'\right]+\frac{1}{3m_2p^2}\left[16K_2''+4K_2'\right]$ $\lambda_4\lambda_5=\frac{1}{m_1m_2}\left(\frac{4K_1}{3}-\frac{8K_2''}{3p^2}-\frac{8K_2'}{3p^2}\right)\left(4K_3'+4K_3''+\frac{12K_2''}{p^2}+\frac{12K_2'}{p^2}\right)+\left(4K_3'+\frac{4K_2''}{p^2}+\frac{8K_2'}{p^2}\right)\left(4K_3''+\frac{8K_2''}{p^2}+\frac{4K_2'}{p^2}\right)\Big]$
K_1 (2)	Consecutive planes parallel to the 111 faces of any one lattice moving along the (111) axis normal thereto in opposite directions while those of the second lattice do the same thing	4	$\lambda_6+\lambda_7=\frac{1}{3\mu}\left(4K_1+\frac{16K_2'}{p^2}+\frac{16K_2''}{p^2}\right)+\frac{8(m_2K_3'+m_1K_3'')}{m_1m_2}$ $\lambda_6\lambda_7=\frac{1}{3m_1m_2}\left(4K_1+\frac{64K_2'}{p^2}+\frac{64K_2''}{p^2}\right)\left(K_1+2K_3'+2K_3''\right)+\frac{8K_1}{m_1m_2}\left(K_3'+K_3''\right)$
M_1 (2)	Same planes as in K_1 now move transverse to the (111) axis and hence acquire twice the degeneracy	8	$\lambda_8+\lambda_9=\frac{4K_1}{3\mu}+\frac{2K_3'}{m_1}+\frac{2K_3''}{m_2}+\frac{1}{3m_1p^2}\left[10K_2''+16K_2'\right]+\frac{1}{3m_2p^2}\left[16K_2''+10K_2'\right]$ $\lambda_8\lambda_9=\frac{1}{m_1m_2}\left[\left(\frac{8K_1}{3}+\frac{8K_2''}{3p^2}+\frac{8K_2'}{3p^2}\right)\left(K_3'+K_3''+\frac{3K_2''}{p^2}+\frac{3K_2'}{p^2}\right)+\left(2K_3'+\frac{2K_2''}{p^2}+\frac{4K_2'}{p^2}\right)\left(2K_3''+\frac{4K_2''}{p^2}+\frac{2K_2'}{p^2}\right)\right]$

coming separately under K_1 and K_3 and M_1 and M_2 in O_h diamond. One distinguishing feature of the T_d structure is the activity of the principal oscillation coming under the F_2 class both in Raman effect and infra-red absorption.

4. *Summary*

Group theoretical methods have been applied for obtaining the normal oscillations of the T_d class diamond structure on the basis of a 16 atom cell as the repeating unit. It is shown that besides the translation, there are nine normal oscillations three of which are threefold degenerate, two of which are fourfold degenerate, two of which are sixfold degenerate and two of which are eightfold degenerate. Expressions are derived for the corresponding normal frequencies by postulating suitable potential energy functions.

REFERENCES

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2. Raman, C. V. .. *Ibid.*, 1944, **19**, 189.