NORMAL OSCILLATIONS OF THE DIAMOND STRUCTURE

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1. *Introduction*

In an earlier paper, Venkatarayudu[1] has used group theoretical methods to show that the primary normal oscillation of the diamond structure consists of a mutual displacement of the two interpenetrating lattices, the direction of displacement being arbitrary. This analysis and similar work in respect of other crystals already published by the author and Venkatarayudu[2] are based on the fundamental assumption that the smallest unit or the Bravais cell of the structure is the repeating pattern both from the static and from the dynamic points of view. That the next stage in the analysis would be to consider a super-lattice of which the cells have twice the edge length of the smallest cell and that the oscillations thus derived would have also to be reckoned in formulating the basic theory of crystal dynamics and of the thermal energy of crystalline solids was pointed out by Raman.[3] In a paper* now under publication, Raman[4] is giving a proper theoretical foundation for the idea of the super-lattice frequencies put forward by him earlier.

In this paper, group theoretical methods are applied to the case of diamond and the results appropriate to a repeating unit which has eight times the volume of the smallest unit cell are given. This 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. Such a cell contains 16 carbon atoms whereas the smallest one contains only 2.

2. *Diamond Structure and its Symmetry Operations*

In Fig. 1 is shown a portion of the diamond structure which is made up of two interpenetrating lattices. The dark circles denote atoms belonging to one lattice whereas the white circles denote the atoms belonging to the other. 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

* An advance copy of this paper has been very kindly sent by Professor Raman to the present author.

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

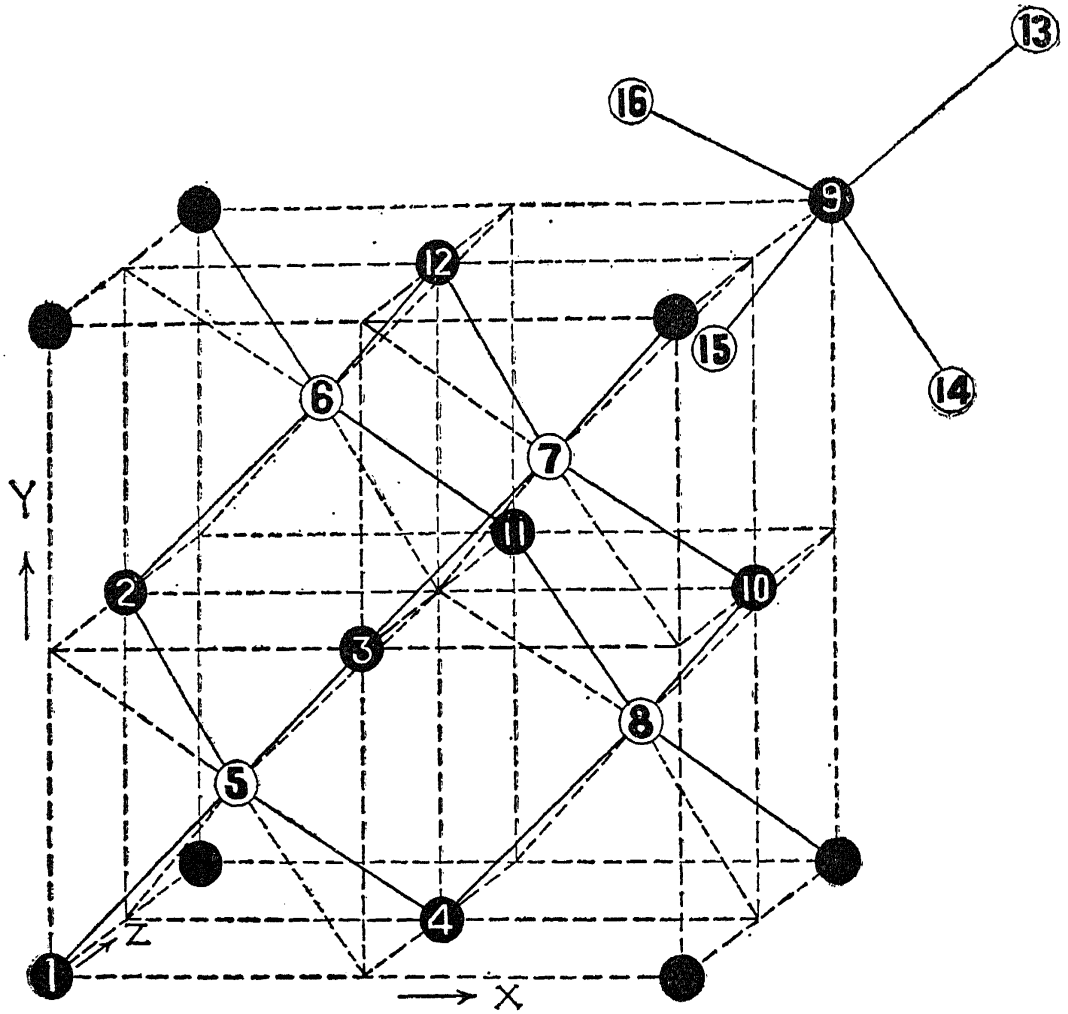

FIG. 1

and all the atoms numbered 2, 3, 4, 9, 10, 11 and 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 48 elements only and has been dealt with earlier. 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 48 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 the diamond structure in which there are 16 non-equivalent points as shown in Fig. 1, will be formed by obtaining the product of the simple 48 elements with the above translational group consisting of 8 elements. The resulting group is of order 384. The elements of this group fall into

	E	32 C_3	12 C_2	12 σ	48 S_4	4 i	32 S_6	24 σ	24 C_2	48 C_4	12 C_2	12 C_2	6 T	24 σ	32 C_3	12 σ	4 i	32 S_6	12 C_2	T	n_t
A_1 ..	1	1	1	1	1	1	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	−1	1	−1	1	1	−1	1	0
A_3 ..	1	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1	1	1	1	−1	−1	−1	1	0
A_4 ..	1	1	1	−1	−1	−1	−1	−1	1	1	1	1	1	−1	1	−1	−1	−1	1	1	0
E_1 ..	2	−1	2	0	0	2	−1	2	0	0	0	2	2	0	−1	0	2	−1	0	2	0
E_2 ..	2	−1	2	0	0	−2	1	−2	0	0	0	2	2	0	−1	0	−2	1	0	2	0
F_1 ..	3	0	−1	−1	1	3	0	−1	−1	1	−1	−1	3	−1	0	−1	3	0	−1	3	0
F_2 ..	3	0	−1	1	−1	3	0	−1	1	−1	1	−1	3	1	0	1	3	0	1	3	1
F_3 ..	3	0	−1	−1	1	−3	0	1	1	−1	1	−1	3	−1	0	−1	−3	0	1	3	0
F_4 ..	3	0	−1	1	−1	−3	0	1	−1	1	−1	−1	3	1	0	1	−3	0	−1	3	1
H_1 ..	6	0	2	2	0	0	0	0	0	0	0	−2	−2	−2	0	2	0	0	0	6	1
H_2 ..	6	0	−2	0	0	0	0	0	2	0	−2	2	−2	0	0	0	0	0	−2	6	1
H_3 ..	6	0	2	−2	0	0	0	0	0	0	0	−2	−2	2	0	−2	0	0	0	6	0
H_4 ..	6	0	−2	0	0	0	0	0	−2	0	2	2	−2	0	0	0	0	0	2	6	1
K_1 ..	4	1	0	2	0	2	1	0	0	0	−2	0	0	0	−1	−2	−2	−1	2	−4	1
K_2 ..	4	1	0	−2	0	2	1	0	0	0	2	0	0	0	−1	2	−2	−1	−2	−4	0
K_3 ..	4	1	0	2	0	−2	−1	0	0	0	2	0	0	0	−1	−2	2	1	−2	−4	1
K_4 ..	4	1	0	−2	0	−2	−1	0	0	0	−2	0	0	0	−1	2	2	1	2	−4	0
M_1 ..	8	−1	0	0	0	4	−1	0	0	0	0	0	0	0	1	0	−4	1	0	−8	1
M_2 ..	8	−1	0	0	0	−4	1	0	0	0	0	0	0	0	1	0	4	−1	0	−8	1
U_R ..	16	4	4	8	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
$h_j x_j$ ..	48	0	−48	96	−96	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	

20 conjugate classes* and the appropriate character table is given here. Notation used is similar to that employed in the earlier papers of the author. The table shows that besides the translation, there are one threefold, three sixfold, two fourfold and two eightfold degenerate normal oscillations coming under various symmetry classes.

If all the last six columns and the last six rows are deleted, we get the character table containing only fourteen conjugate classes and if the number of elements in each conjugate class is properly adjusted, we get results that are appropriate to a group of 192 elements which refers to the case where the smallest cubic cell containing 8 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.

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

$$(x_1+x_2)-(x_3+x_4)+(x_9+x_{10})-(x_{11}+x_{12}) \quad .. \quad .. \quad .. \quad H_1$$

$$(x_1-x_2+x_3-x_4)+(y_5-y_6+y_7-y_8)+(x_9-x_{10}+x_{11}-x_{12}) + (y_{13}-y_{14}+y_{15}-y_{16}) \quad .. \quad .. \quad .. \quad .. \quad .. \quad H_2$$

$$(x_1-x_2+x_3-x_4)-(y_5-y_6+y_7-y_8)+(x_9-x_{10}+x_{11}-x_{12}) - (y_{13}-y_{14}+y_{15}-y_{16}) \quad .. \quad .. \quad .. \quad .. \quad .. \quad H_4$$

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

$$(p_2+p_3+p_4-p_6-p_7-p_8+p_9-p_{13}) - (p_1-p_5+p_{10}+p_{11}+p_{12}-p_{14}-p_{15}-p_{16}) \quad .. \quad .. \quad .. \quad K_3$$

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

$$-(x_1-z_1)+(x_2-z_2+x_3-z_3+x_4-z_4)+(x_9-z_9)-(x_{10}-z_{10} + x_{11}-z_{11}+x_{12}-z_{12})+(x_5-z_5)-(x_6-z_6+x_7-z_7+x_8-z_8) - (x_{13}-z_{13})+(x_{14}-z_{14}+x_{15}-z_{15}+x_{16}-z_{16}) \quad .. \quad .. \quad M_2$$

* Writing down all the 384 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.

† This case had been fully worked out last year by the author in collaboration with Dr. T. Venkatarayudu but the results remained unpublished.

In K_1 and K_3, p stands for a displacement x, y, z. 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.

	Mode	*Degeneracy*	$4\pi^2\nu^2$
F_2	One interpenetrating lattice oscillating against the other.	3	$\frac{8K_1}{3m}+\frac{64K_2}{3mp^2}$
H_1	Consecutive planes parallel to the cube faces of any one lattice moving along the cubic axis normal thereto in opposite directions.	6	$\frac{4K_1}{3m}+\frac{40K_2}{3mp^2}+\frac{8K_3}{m}$
H_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 but in phase.	6	$\frac{12K_2}{mp^2}+\frac{4K_3}{m}$
H_4	,, ,, ,, while those of the second lattice do the same thing but in opposite phase.	6	$\frac{8K_1}{3m}+\frac{4K_2}{3mp^2}+\frac{4K_3}{m}$
K_1	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 but in phase.	4	$\frac{2K_1}{3m}+\frac{64K_2}{3mp^2}+\frac{8K_3}{m}$
K_3	,, ,, ,, while those of the second lattice do the same thing but in opposite phase.	4	$\frac{2K_1}{m}+\frac{8K_3}{m}$
M_1	Same planes as in K_1 now move transverse to the (111) axis and hence acquire twice the degeneracy.	8	$\frac{8K_1}{3m}+\frac{34K_2}{3mp^2}+\frac{2K_3}{m}$
M_2	Same as in M_1 but planes belonging to the two lattices are in opposite phase.	8	$\frac{6K_2}{mp^2}+\frac{2K_3}{m}$

K_1 and K_3 are respectively the force constants referring to any pair of atoms which constitute the nearest neighbours and the next nearest neighbours. K_2 represents the force called into play when the angle between any two valence bonds which meet at an atom varies. p stands for the distance between a pair of nearest neighbours and is the same as the length of the valence bond.

In conclusion, the author desires to express his thanks to Sir C. V. Raman with whom he had the opportunity of discussing this subject on several occasions.

Summary

Group theoretical methods have been applied for obtaining the normal oscillations of the diamond structure on the basis of a 16 atom cell as the repeating unit. It is shown that besides the translation, there are eight normal oscillations one of which is threefold degenerate, two of which are fourfold degenerate, three 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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3. Raman, C. V. .. *Ibid.*, 1941, **14**, 459.
4. ——— .. *Ibid.*, 1943, **18**, 237.