

# THE FREQUENCY SPECTRUM OF THE DIAMOND LATTICE

BY E. V. CHELAM

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received November 2, 1943

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

## 1. Introduction

THE many remarkable physical properties which diamond exhibits and the fact that the element carbon of which it is a crystalline form occupies a unique position in the field of chemistry invest this substance with an altogether exceptional interest for the experimental physicist. There is good reason why the mathematical physicist should also regard diamond with special interest. It is the typical valence crystal, and as it belongs to the cubic system and has a relatively simple structure, its physical behaviour should be readily amenable to theoretical explanation and computation. Indeed, the diamond lattice may fairly be regarded as a test case for any theory of the solid state.

Ramaswamy (1930) observed a sharp and intense line with a frequency shift of  $1332\text{ cm.}^{-1}$  in the Raman spectrum of diamond and interpreted the same as the "rest-strahlen frequency" of diamond. He established the correctness of this interpretation by showing that the observed frequency agrees perfectly with that calculated from the Nernst-Lindemann specific heat formula and less perfectly with the Debye "limiting frequency" for diamond. Ramaswamy also discussed the reason for the appearance of the rest-strahlen frequency as a Raman-shift in diamond, as contrasted with its non-appearance in the alkali halides. Ramaswamy's claim that  $1332\text{ cm.}^{-1}$  is the fundamental vibration frequency of the diamond lattice has been fully confirmed by the theoretical work of Nagendra Nath (1934), Venkatarayudu (1938) and of Bhagavantam and Venkatarayudu (1939). Their investigations have made it clear that an oscillation of the two interpenetrating lattices of carbon atoms with respect to each other would have this frequency and that it would be active in the Raman effect.

Other experimental facts have however awaited a satisfactory explanation. Amongst these should be specially mentioned the observation by Bhagavantam (1930) of several other feeble lines in the Raman spectrum

of diamond with frequency shifts both larger and smaller than  $1332\text{ cm.}^{-1}$ , the strongest of them having a frequency shift of  $1158\text{ cm.}^{-1}$ . The significance of this observation as well as of the infra-red absorption data for diamond recorded by Julius, Angstrom, Reinkober (1911) and Robertson and Fox (1930) was far from being clear. To throw some light on these matters, Dr. Nagendra Nath (1937-40) made an elaborate investigation of the frequency spectrum of the diamond on the basis of the Born theory. His results however remained unpublished.

The subject entered on a new phase as the result of the investigations by P. G. N. Nayar (1941, 1942) of the luminescence and associated absorption spectra of diamond at liquid air temperatures. Nayar worked with some of the diamonds in the extensive collection made by Sir C. V. Raman, and his results showed conclusively that the lattice spectrum of diamond contains a whole series of *discrete* frequencies stretching from  $1332\text{ cm.}^{-1}$  downwards to quite low values. To explain these results of Nayar, Sir C. V. Raman (1941) put forward a new theory of the lattice vibrations in crystals, the basis of which was the postulate that these vibrations are *repetitive patterns in space*, the unit of the pattern having dimensions either identical with or an integral multiple of the dimensions of the lattice cell in the crystal. This idea has received a precise mathematical form and a dynamical justification in the introductory paper of the present symposium by Sir C. V. Raman. It is there shown that a super-cell whose dimensions are twice as great as those of a lattice cell is the space-unit of the repetition-pattern of the atomic vibrations properly so called, while vibrations whose repetitive units are of still larger dimensions fall in the category of elastic vibrations.

The various modes of atomic vibration possible in diamond on the basis of the Raman theory have already been derived and discussed in an earlier paper by the present author appearing in the symposium. It will now be shown how an expression for their frequencies may be derived on the basis of a scheme of force-constants similar to that employed by Nagendra Nath and others in their investigations.

## 2. The Geometry of the Lattice

To enable us to proceed we require a suitable notation for the atoms in the lattice and their displacements. The eight atoms in the unit cube have the following positions:

1	2	3	4	
$(0, 0, 0)$	$(0, \frac{1}{2}, \frac{1}{2})$	$(\frac{1}{2}, 0, \frac{1}{2})$	$(\frac{1}{2}, \frac{1}{2}, 0)$	
5	6	7	8	(1)
$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	$(\frac{1}{4}, \frac{3}{4}, \frac{3}{4})$	$(\frac{3}{4}, \frac{1}{4}, \frac{3}{4})$	$(\frac{3}{4}, \frac{3}{4}, \frac{1}{4})$	

Atoms 2, 3, 4 can be obtained by primitive translations from 1 and 6, 7, 8 likewise from 5. The rotational and reflexional symmetry of the lattice is represented by 48 operations of the octahedral group. There are actually only two non-equivalent atoms in the lattice, 1 and 5, and these may be regarded as representative of two lattice systems. Each atom of a system is surrounded tetrahedrally by four atoms of the opposite system. These are its nearest neighbours. The next nearest neighbours of an atom are twelve in number and they come from the same system. Four atoms of type 2, four of type 3, and four of type 4 are the next nearest neighbours of 1. As an illustration, we give here all the next nearest neighbours of atom 5. Let us introduce operations  $t_x, t_y, t_z$  for translations through  $(a, 0, 0)$ ;  $(0, a, 0)$ ;  $(0, 0, a)$ ,  $a$  being the length of the edge of an 8-atom cell. By combining these operations we can form a set of operations  $t_x, t_y, t_z, t_y t_x, t_x t_y$  and  $t_x t_y t_z$ , eight in number. These carry the 8-atom cell in fact into the 8 cells of a supercell containing 64 atoms.  $\bar{t}_x$  will be a translation through an opposite direction, *i.e.*, through  $(-a, 0, 0)$ . The symbol  $5(t_x)$  may be used to denote an atom obtainable from 5 by the translation  $t_x$ . Similar notation can be used to denote for 6, 7, 8, etc. With this notation, the twelve next nearest neighbours of the atom can be indicated below as

$$\begin{aligned} 6_1 &= 6(\bar{t}_y \bar{t}_z); & 6_2 &= 6; & 6_3 &= 6(\bar{t}_y); & 6_4 &= 6(\bar{t}_z) \\ 7_1 &= 7(t_x \bar{t}_x); & 7_2 &= 7(\bar{t}_x); & 7_3 &= 7; & 7_4 &= 7(\bar{t}_z) \\ 8_1 &= 8(\bar{t}_x \bar{t}_y); & 8_2 &= 8(\bar{t}_x); & 8_3 &= 8(\bar{t}_y); & 8_4 &= 8. \end{aligned} \quad (2)$$

The notation  $6_1, 7_2, 8_3$ , etc., is very convenient and has been borrowed from Dr. Nagendra Nath's unpublished work. We are now in a position to illustrate how the normal modes can be derived.

### 3. The Equations of Motion

It has been explained in another paper that in a normal mode, it is sufficient to know the displacements of one atom and the relative displacements of the other atoms. These displacements are known when the normal co-ordinate is known. Further, in a normal mode all the atoms move with the same frequency. It is therefore sufficient to consider the equation of motion of a single atom. The kinetic energy of atom 5 is  $2T = m(\dot{x}_5^2 + \dot{y}_5^2 + \dot{z}_5^2)$ , all co-ordinates being displacements from the equilibrium position and parallel to the cubic axes. Since the equations of motion involve the derivative of the potential energy function with respect to  $x_5, y_5$ , or  $z_5$  it is enough if we consider terms of the potential energy involving these only. The energy function chosen in this case represents the valence forces, forces of angular distortion and interaction between the next nearest neighbours. Accordingly,

potential energy terms involving atom 5 can be represented as

$$2V = K (d_{15}^2 + d_{25}^2 + d_{35}^2 + d_{45}^2) + K_\alpha (\theta_{23}^2 + \theta_{31}^2 + \theta_{12}^2 + \theta_{14}^2 + \theta_{24}^2 + \theta_{34}^2) + K_\alpha \sum_{r=1}^{12} \phi_{r5}^2 + K'' \sum_{r=1}^{12} D_{r5}^2. \quad (3)$$

The summation in the last two terms runs over the next nearest neighbours of atom 5.  $d_{15}$  represents the variation in the distance 1-5 while  $D_{r5}$  is the variation in the distance between atom 5 and one of its nearest neighbours, the atom  $r$ .  $\theta_{rs}$  denotes the variation in the angle subtended at 5 by the atom ' $r$ ' and ' $s$ '.  $\phi_{r5}$  denotes the variation in angle subtended by the atom ' $r$ ' and 5 at the appropriate atom. In terms of cartesian co-ordinates, these are given by

$$d_{rs} = (x_r - x_s) \xi_{rs} + (y_r - y_s) \eta_{rs} + (z_r - z_s) \zeta_{rs} \quad (4)$$

and the same type of expressions for  $D_{rs}$ . Here  $\xi_{rs}$ ,  $\eta_{rs}$ ,  $\zeta_{rs}$  are the direction cosines of the lines joining the ' $r$ 'th atom to the ' $s$ 'th atom. If  $(a_r, b_r, c_r)$  and  $(a_s, b_s, c_s)$  are their positional co-ordinates, and  $l_{rs}$  the distance between them

$$\xi_{rs} = \frac{a_r - a_s}{l_{rs}}, \quad \eta_{rs} = \frac{b_r - b_s}{l_{rs}}, \quad \zeta_{rs} = \frac{c_r - c_s}{l_{rs}}. \quad (5)$$

We also have,

$$p \theta_{rs} = \sqrt{3} d_{rt} - \sqrt{2} (d_{st} + d_{st}), \quad (6)$$

where  $p$  is the distance between nearest neighbours in equilibrium configuration and ' $t$ ' denotes the suffix of the atom at which ' $r$ ' and ' $s$ ' subtend the valence angle. Similar expressions hold for  $\phi_{rs}$ . These relations enable us to write down the Hamiltonian in terms of cartesian co-ordinates and form the equations of motion. Differentiating the potential energy function and equating the rate of change of momentum to it, we get the following equation of motion for  $x_5$ .

$$\begin{aligned} -m \ddot{x}_5 &= \lambda x_5 = P x_5 - Q (x_1 + x_2 + x_3 + x_4) + S (x_{6_1} + x_{6_2} + x_{6_3} + x_{6_4}) \\ &- U (x_{7_1} + x_{7_2} + x_{7_3} + x_{7_4} + x_{8_1} + x_{8_2} + x_{8_3} + x_{8_4}) \\ &- R (y_1 - y_2 - y_3 + y_4 + z_1 - z_2 + z_3 - z_4) \\ &- V (y_{6_1} - y_{6_2} - y_{6_3} + y_{6_4} + z_{6_1} - z_{6_2} + z_{6_3} - z_{6_4}) \\ &+ V (y_{7_1} - y_{7_2} - y_{7_3} + y_{7_4} + z_{8_1} - z_{8_2} + z_{8_3} - z_{8_4}) \\ &- U (y_{8_1} - y_{8_2} - y_{8_3} + y_{8_4} + z_{7_1} - z_{7_2} + z_{7_3} - z_{7_4}) \end{aligned} \quad (7)$$

where  $\lambda = (2\pi\nu)^2 m$ ,  $m$  being the mass of the carbon atom and  $\nu$  the frequency.

$$\begin{aligned} P &= \frac{4}{3} (K + 7 K_\alpha + 3K''), \quad Q = \frac{1}{3} (K + 8 K_\alpha), \quad R = \frac{1}{3} (K - 4 K_\alpha), \\ S &= \frac{2K_\alpha}{3}, \quad U = \frac{K_\alpha}{6} + \frac{K''}{2}, \quad V = -\frac{K_\alpha}{3}. \end{aligned} \quad (8)$$

## 4. The Expressions for the Frequencies

Once the equation of motion for  $x_5$  is written out, we can substitute in it the known relative displacements of the other atoms in any chosen normal mode. The normal mode completely specifies the displacements of every atom in the cell in terms of  $x_5$  and putting the values in (7) we get an expression for  $\nu$ , the frequency. Among the normal modes we need pick out for consideration only eight, with only one each from a set of mutually equivalent degenerate modes. There are only eight such distinct frequencies and taking the cases one by one the expressions will be calculated. A knowledge of the normal co-ordinates is assumed here and can be easily taken over from earlier papers.

(1, 1, 1) vector.  $\chi(t_x) = \chi(t_y) = \chi(t_z) = 1$ ;

$$x_5 = x_6 = x_7 = x_8 = x_{5_1} = x_{6_1} = \text{etc.}, = x_{8_1} = x_{8_2} = \text{etc.}, \\ = -x_1 = -x_2 = -x_3 = -x_4 = \text{etc.}$$

as all the eight super-cells go the same way, with the lattice systems 1 and 5 going the opposite ways. The  $y$  and  $z$  displacements are zero; substituting these we get

$$\lambda_1 = \frac{8K + 64K_\alpha}{3m}; \quad \text{Degeneracy 3.}$$

(-1, -1, -1) vector.

$$\chi(t_x) = \chi(t_y) = \chi(t_z) = -1.$$

Therefore  $-u_5 = u_{6_1} = u_6 = -u_{6_2} = -u_{6_3} = u_7 = u_8$ , etc.,

and correspondingly for  $u_1, u_2$ , etc.  $u = x, y$ , or  $z$ .

These relations hold for all frequencies of this vector.

$\lambda_2$  corresponds to the motion of alternate (1, 1, 1) planes normal to themselves.

Here  $x_1 = y_1 = z_1 = -x_5 = -y_5 = -z_5$

with the relative displacements of the other atoms defined as above.

Substituting

$$\lambda_2 = \frac{2K + 8K''}{m}; \quad \text{Degeneracy 4}$$

$$\lambda_3 \text{ is defined by } x_1 = y_1 = z_1 = x_5 = y_5 = z_5: \quad \text{Degeneracy 6}$$

$$\lambda_3 = \frac{2}{3m} (K + 32K_\alpha + 12K'')$$

$$\lambda_4 \text{ is defined by } z_1 = -x_1 = -z_5 = x_5: \quad \text{Degeneracy 8}$$

$$\lambda_4 = \frac{8K + 34K_\alpha}{3m} + \frac{2K''}{m}$$

$$\lambda_5 \text{ is defined by } z_1 = -x_1 = z_5 = -x_5: \quad \text{Degeneracy 8}$$

$$\lambda_5 = \frac{6K_\alpha + 2K''}{m}.$$

In these modes the relative displacements of all the atoms equivalent to 1 or 5 must be derived from the characteristic relations defined by the vector (1, 1, 1). On substituting all these, the expressions given above are obtained. (1, -1, -1) vector

$$\lambda_6 \text{ defined by } x_5 = x_6 = -x_7 = -x_8$$

$$\lambda_6 = \frac{4K + 40K_a}{3m} + \frac{8K''}{m} : \quad \text{Degeneracy 6.}$$

The motion of the rest of the atoms is defined by the above vector.

For  $\lambda_7$  and  $\lambda_8$  involving motions in tangential directions there is no displacements of the x co-ordinate so far as this vector is concerned. Since we have written down the equation for  $x_5$ , it is convenient to consider the (-1, 1, -1) or (-1, -1, 1) vectors for  $\lambda_7$  and  $\lambda_8$ .

$$z_1 = -z_2 = z_3 = -z_4 = x_5 = -x_6 = x_7 = -x_8$$

$$\text{and } z_1 = -z_2 = z_3 = -z_4 = -x_5 = x_6 = -x_7 = x_8$$

define the two modes for (-1, 1, -1) vector. Substituting these relations, we get

$$\lambda_7 = \frac{12K_a + 4K''}{m} : \quad \text{Degeneracy 6}$$

$$\lambda_8 = \frac{8K + 4K_a}{3m} + \frac{4K''}{m} : \quad \text{Degeneracy 6}$$

This completes all the 8 frequencies. We finally present in a tabular form all the 8 frequencies with their degeneracies.

Frequency Number	Description	Magnitude	Degeneracy
$\lambda_1$	Two lattices moving oppositely	$\frac{8K + 64K_a}{3m}$	3
$\lambda_2$	Motion of alternate sets of octahedral planes as fully explained in earlier papers	$\frac{2K + 8K''}{m}$	4
$\lambda_3$		$\frac{2}{3m} (K + 32K_a + 12K'')$	4
$\lambda_4$		$\frac{8K + 34K_a + 2K''}{3m}$	8
$\lambda_5$		$\frac{6K_a + 2K''}{m}$	8
$\lambda_6$	Motion of alternate cubic planes as explained in earlier papers	$\frac{4K + 40K_a}{3m} + \frac{8K''}{m}$	6
$\lambda_7$		$\frac{12K_a + 4K''}{m}$	6
$\lambda_8$		$\frac{8K + 4K_a}{3m} + \frac{4K''}{m}$	6

The author has the greatest pleasure in acknowledging his indebtedness to Sir C. V. Raman, Kt., F.R.S., N.L., for his kind suggestions and constant encouragement during the course of this work. The author is also extremely obliged to his professor, Dr. N. S. Nagendra Nath, M.Sc., Ph.D., under whose direction and guidance a very considerable part of this work was conducted. The notation has also been borrowed from his unpublished work. He also wishes to express his thanks to Prof. S. Bhagavantam for his kind interest in this work.

### *Summary*

The eight frequencies in a diamond lattice are calculated with a suitable force field and explicit expressions are given for them. Sir C. V. Raman's theory of superlattice vibrations is the basis of the investigation.

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