

# THE CHARACTERISTIC VIBRATIONS OF CRYSTAL LATTICES—PART I

BY K. S. VISWANATHAN

*(From the Raman Research Institute, Bangalore)*

Received December 23, 1952

*(Communicated by Sir C. V. Raman, F.R.S., N.I.)*

## A. INTRODUCTION

THE importance of the knowledge of the different modes of atomic vibrations of a crystal, which constitutes the core of any theory on the thermal and optical behaviour of solids, needs hardly to be stressed. The first great step towards a proper theory on the thermal energy of solids was undertaken by Einstein who evaluated the specific heat of crystals on the assumption that the different atoms of the crystals are independent oscillators, each contributing the same amount to its thermal energy. The later theory of Debye rests on the assumption that the proper vibrations of the atoms of the crystal can be identified with the different modes of vibrations of an elastic body and as such seeks to replace their thermal energy with the energy content of elastic bodies. While the Debye theory clearly ignores the lattice structure of crystals and the atomic constitution of matter, these were taken into account in the theory of Born-Karman<sup>1</sup> which was proposed almost simultaneously (1913). The Born lattice dynamics sought to enumerate the different normal modes of vibrations of a crystal composed of  $N$  atoms and postulated the existence of a total number of  $(3N-3)$  frequencies, forming a continuous spectrum spread over a wide range of frequencies. On this basis, each degree of freedom of the system corresponds to a wave whose wavelength is determined by the cyclic boundary conditions. An attempt to apply the Born-Karman theory to some simple cases of cubic crystals was made by Blackman<sup>2</sup> who reported the presence of several maxima in the frequency spectrum; but still no qualitative description on the nature of the frequency spectrum of a general crystal is available in the literature. On the other hand, the application of the theory to any physical problem involving quantitative calculations is severely complicated so that the attempts to make progress in this direction have not been successful, even with several simplifying assumptions regarding the nature of the inter-atomic forces.

An entirely different approach to the problem, considering the movements of the individual atoms as distinct from a wave that progresses through it, was made by Sir C. V. Raman (1943).<sup>3,4</sup> This theoretical procedure predicts, for a crystal with  $p$  atoms in each of its unit cells, the presence of a discrete set of  $(24p-3)$  monochromatic frequencies, which are observable as sharply defined lines either in the first-order or the second-order Raman spectrum. In addition, the high frequency spectrum of these normal vibrations representing the internal oscillations of its unit cells, should be supplemented by an elastic spectrum, continuous in nature and which is a consequence of the translatory movements of its lattice cells.

Assuming the existence of waves that travel through the same type of atoms in the lattice arrangement of the crystal and with no special restrictive assumptions either on the nature of the interacting forces or on the structure of the lattice cells, it is shown in this paper that the group velocity of these waves vanishes for  $(24p-3)$  frequencies, which are characteristic of the crystal structure. In Part II of this paper, it is proved that the state of disturbance in the crystal arising out of an initial disturbance confined to a small region of it tends asymptotically to a superposition of these  $(24p-3)$  characteristic vibrations. These results clearly show that even a picture of an infinity of waves through the crystal and consequently of frequencies associated with them leads, naturally to the conclusion that only a discrete set of  $(24p-3)$  normal vibrations, as conceived by Sir C. V. Raman, are physically significant; the effect of the elastic waves which (at ordinary temperatures) contribute in much lesser a measure to the vibrational energy of the crystal can be accounted for by an elastic spectrum of the Debye type, but with a greatly reduced proportion of the degrees of freedom associated with it.

### 1. THE EQUATIONS OF MOTION

We consider a crystal consisting of  $p$  atoms in each of its unit cells and denote the displacements of any atom parallel to the three mutually orthogonal co-ordinate axes  $x^i$  by  $q_{irs}$  ( $i = 1, 2, 3$ ). Throughout this paper, we use the letters  $r$  and  $\rho$  exclusively to represent the index number of a particular atom among the  $p$  atoms in any cell, while  $\sigma$  and  $s$  will be used to indicate the cell number of the crystal.

The general equations of motion for the atoms of the lattice and the relationship between the force constants occurring in the most general form of the potential energy expression, were given by Raman and Born. For the sake of completeness, these results are quoted here. If  $m_r$  denotes the

mass of the  $r$ th atom in any cell, the expressions for the kinetic and potential energies are given by

$$2T = \sum_{irs} m_r \dot{q}_{irs}^2 \quad (1)$$

$$2V = \sum_{irs} \sum_{j\rho\sigma} k_{irs}^{j\rho\sigma} q_{irs} q_{j\rho\sigma}$$

If  $\mathbf{d}_1, \mathbf{d}_2, \mathbf{d}_3$  be the three primitive translational vectors of the crystal lattice, then the position of any cell of the crystal is specified by the vector  $\mathbf{s} = (s_1, s_2, s_3)$  or  $\mathbf{s} = s_1\mathbf{d}_1 + s_2\mathbf{d}_2 + s_3\mathbf{d}_3$ . Two cells  $\sigma_i$  and  $\sigma_j$  will hereafter be called *conjugate* with respect to the cell  $\mathbf{s}$  if

$$\sigma_i - \mathbf{s} = \mathbf{s} - \sigma_j \quad (2)$$

The *group* property implied in the translational symmetry of the crystal yields now the following relations between the force constants involved in the expression (1).

$$\begin{aligned} (a) \quad k_{irs}^{j\rho\sigma} &= k_{j\rho\sigma}^{irs} \\ (b) \quad k_{irs}^{irs} &= k_{irs'}^{irs'} \\ (c) \quad k_{irs}^{j\rho\sigma} &= k_{irs'}^{j\rho\sigma'} \end{aligned} \quad (3)$$

where  $(s, s')$  and  $(\sigma, \sigma')$  denote two pairs of cells given by  $\mathbf{s} - \mathbf{s}' = \sigma - \sigma'$ .

Since the interatomic forces are quite short-ranged, the force constants diminish rapidly with distance and we restrict the interaction of any atom in the cell  $\mathbf{s}$  to all the atoms in the  $2N + 1 = \prod_{r=1,2,3} (2l_r + 1)$  surrounding cells given by  $\sigma = \mathbf{s} + \mathbf{k}$ ;  $\mathbf{k} = (k_1, k_2, k_3)$  where  $k_1, k_2, k_3$  assume all integral values in the intervals  $\pm l_1$ ;  $\pm l_2$ ; and  $\pm l_3$  respectively.

The equations of motion of the particles in the  $r$ th cell can now be written as

$$-m_r \ddot{q}_{irs} = \sum_{j, \rho, \sigma} k_{irs}^{j\rho\sigma} q_{j\rho\sigma} \quad (4)$$

$$\left( \begin{array}{l} i = 1, 2, 3 \\ r = 1, 2, \dots, p \end{array} \right)$$

We shall assume wave solutions for the above equations of the form

$$q_{irs} = A_r^i e^{i(\omega t + \mathbf{a} \cdot \mathbf{s})} \quad (5)$$

where  $\mathbf{a}$ , considered to be a vector of the reciprocal lattice, denotes the wave vector. If  $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$  denote the three fundamental vectors of the reciprocal lattice, then we can write

$$\mathbf{a} = \theta_1 \mathbf{b}_1 + \theta_2 \mathbf{b}_2 + \theta_3 \mathbf{b}_3 \text{ so that we have}$$

$$\mathbf{a} \cdot \mathbf{s} = \sum_{i=1}^3 s_i \theta_i \text{ since } \mathbf{b}_i \cdot \mathbf{d}_j = \delta_{ij}. \quad (6)$$

Substituting (5) in (4) we get the following  $3p$  equations linear in the  $A$ 's

$$A_{r'}^i (k_{irs}^{irs} + \sum_{\sigma} k_{irs}^{irs} e^{i\alpha \cdot (\sigma-s)} - m_r \omega^2) + \sum_{\rho, j} A_{\rho}^j (k_{irs}^{j\rho s} + \sum_{\sigma} k_{irs}^{j\rho \sigma} e^{i\alpha \cdot (\sigma-s)}) = 0 \quad (7)$$

the accent indicating that the term  $\rho = r; j = i$  is omitted in the summation of the second term and the summation for  $\sigma$  covers the  $2N$  surrounding cells of  $s$ .

We shall now arrange the  $3p$  terms in each of the above  $3p$  equations into  $p$  groups in *lexical* order with respect to the letter  $\rho$ , the three terms in each group involving the quantities  $A_{\rho}^i$  ( $i = 1, 2, 3$ ) themselves being arranged in increasing order with respect to the index  $i$ . Then if,

$$\left. \begin{aligned} s' &= 3(r-1) + i \\ t' &= 3(\rho-1) + j \end{aligned} \right\} i, j = 1, 2, 3$$

and  $a_{s't'} = k_{irs}^{j\rho s} + \sum_{\sigma} k_{irs}^{j\rho \sigma} e^{i\alpha \cdot (\sigma-s)}$ , we get on eliminating the  $A$ 's from (7) the following equation, due to Born.

$$|A - M\omega^2| = 0, \quad (8)$$

where  $A$  denotes the matrix  $(a_{s't'})$  and  $M$ , the diagonal matrix defined by  $m_{s's'} = m_r$ .

## 2. THE GROUP VELOCITY OF THE WAVES

We can now easily see that the matrix  $(A)$  is hermitian. For, if  $\sigma_1$  and  $\sigma_2$  denote any two cells conjugate to the cell  $s$ , then from (3) we get

$$\begin{aligned} k_{irs}^{j\rho \sigma_1} &= k_{irs}^{j\rho \sigma_2} = k_{j\rho s}^{i\sigma_2} \text{ and so} \\ k_{irs}^{j\rho \sigma_1} e^{i\alpha \cdot (\sigma_1-s)} &= k_{j\rho s}^{i\sigma_2} e^{i\alpha \cdot (s-\sigma_2)} \\ \therefore a_{s't'} &= k_{irs}^{j\rho s} + \sum_{\sigma} k_{irs}^{j\rho \sigma} e^{i\alpha \cdot (\sigma-s)} \\ &= k_{j\rho s}^{irs} + \sum_{\sigma} k_{j\rho s}^{i\sigma} e^{i\alpha \cdot (s-\sigma)} = \bar{a}_{t's'} \end{aligned} \quad (9)$$

for the  $2N$  cells over which the summation for  $\sigma$  extends, can be split up into  $N$  pairs of conjugate cells.

Letting  $z = \omega^2$ , we rewrite (8) as

$$s_0 z^{3p} + s_1 z^{3p-1} + \dots + s_t z^{3p-t} + \dots + s_{3p-1} z + s_{3p} = 0 \quad (10)$$

If  $m_{s'} = m_r \binom{s' = 3(r-1) + i}{i = 1, 2, 3}$ , then the coefficients  $s_0, \dots, s_{3p}$  are given by the following scheme.

$$\begin{aligned} s_0 &= (-1)^{3p} (m_1 m_2 \dots m_p)^3. \\ s_1 &= (-1)^{3p-1} (m_1 m_2 \dots m_p)^3 \sum_{i,r} \frac{a_{s's'}}{m_r}. \\ s_t &= (-1)^{3p-t} \sum m_{s_1'} m_{s_2'} \dots m_{s_t'} B \end{aligned} \quad (11 a)$$

where B is a principal minor of order  $t$ , which is the complementary minor of the determinant formed from the elements of the rows  $s_1', s_2', \dots, s_k'$  ( $k = 3p - t$ ) of the determinant A and the summation extends over the  $({}^{3p}C_t)$  principal minors of order  $t$  of  $|A|$ . In virtue of the hermitian property of (A), the principal minors of (A) are themselves hermitian and their determinants are therefore real. In particular, we have  $s_{3p} = |A|$ , the determinant of the matrix (A). While the reality of the roots of (9) follows immediately from the hermitian form of A, they should in addition be positive because of the positive nature of the potential energy expression.

If  $a$  denotes the absolute magnitude of the wave vector  $\mathbf{a}$  so that  $\mathbf{a} = ea$ ,  $\mathbf{e}$  being a directional unit vector, then the group velocity of the waves is given by  $\frac{d\omega}{da}$ . Equation (10) is of degree  $3p$  in  $z$  and if its roots are denoted by  $z_k = \omega_k^2$  ( $k = 1, 2, \dots, 3p$ ), we get on differentiating (10) with respect to  $a$ ,

$$2\omega_k \frac{d\omega_k}{da} \left( \sum_{t=0}^{3p-1} (3p-t) s_t z_k^{3p-t-1} \right) = - \left( \sum_{t=1}^{3p} z_k^{3p-t} \frac{ds_t}{da} \right) \quad (11)$$

Denoting the cofactor of  $a_{s't'}$  in  $|A|$  by  $A_{s't'}$  we have now

$$\begin{aligned} \frac{ds_{3p}}{da} &= \sum_{s', t'} \frac{da_{s't'}}{da} A_{s't'} \\ &= \sum_{s'=1}^{3p} \frac{da_{s's'}}{da} A_{s's'} + \sum_{\substack{s', t' \\ s' < t'}} \left\{ \frac{da_{s't'}}{da} A_{s't'} + \frac{da_{t's'}}{da} A_{t's'} \right\} \\ &= \sum_{s'=1}^{3p} \frac{da_{s's'}}{da} A_{s's'} + 2 \sum_{s' < t'} R \left( \frac{da_{s't'}}{da} A_{s't'} \right) \end{aligned} \quad (12)$$

since  $A_{s't'}$  and  $A_{t's'}$  are also complex conjugates.

$$\text{Now } \frac{da_{s's'}}{da} = -2 \sum_{\sigma_i} k_{irs}^{\sigma_i} \mathbf{e} \cdot (\boldsymbol{\sigma}_i - \mathbf{s}) \sin \mathbf{a} \cdot (\boldsymbol{\sigma}_i - \mathbf{s})$$

the summation here being over a set of  $N$  non-conjugate cells.

If  $\sigma_i = \mathbf{s} + \mathbf{k}_i$  where  $\mathbf{k}_i = (k_i^1, k_i^2, k_i^3)$ , then  $\mathbf{a} \cdot (\sigma_i - \mathbf{s}) = \sum_{j=1}^3 k_i^j \theta_j$  and  $\sin \mathbf{a} \cdot (\sigma_i - \mathbf{s})$  will be equal to zero whenever  $\theta_1, \theta_2$  and  $\theta_3$  each assumes any one of the values 0 or  $\pi$ . Hence  $\frac{da_{s's'}}{da}$  vanishes for the set of points (0, 0, 0); (0,  $\pi$ , 0); (0, 0,  $\pi$ ); ( $\pi$ , 0, 0); (0,  $\pi$ ,  $\pi$ ); ( $\pi$ , 0,  $\pi$ ); ( $\pi$ ,  $\pi$ , 0) and ( $\pi$ ,  $\pi$ ,  $\pi$ ) in the  $\theta$ -space. (13)

If  $\frac{da_{s't'}}{da} = x + iy$  and  $A_{s't'} = x' + iy'$ , then  $R \left( \frac{da_{s't'}}{da} A_{s't'} \right) = (xx' - yy')$ .

Now, each term in the expression for  $y'$  contains at least one factor of the type  $\sum_{\sigma} k_{irs}^{i\rho\sigma} \sin \mathbf{a} \cdot (\sigma - \mathbf{s})$  and  $A_{s't'}$  is real if each one of the quantities  $\theta_1, \theta_2$  and  $\theta_3$  takes the values 0 or  $\pi$ . Further,

$$x = - \sum_{\sigma} k_{irs}^{i\rho\sigma} \mathbf{e} \cdot (\sigma - \mathbf{s}) \sin \mathbf{a} \cdot (\sigma - \mathbf{s}).$$

Hence  $R \left( \frac{da_{s't'}}{da} A_{s't'} \right)$  and consequently  $\frac{ds_{3\beta}}{da}$  which is a function of the  $\theta$ 's vanishes at the set of eight points given in (13).

Since the principal minors of order  $t$  of  $A$  are themselves hermitian, a similar argument applies to each determinant  $|B|$  in (11 a) and we get

$$\frac{ds_t}{da} = 0 \quad (t = 1, 2, \dots, 3p) \quad (14)$$

if  $\theta_1 = 0$  or  $\pi$ ;  $\theta_2 = 0$  or  $\pi$ ;  $\theta_3 = 0$  or  $\pi$ .

It follows therefore from (11) that the group velocity of the waves associated with each of the eight points of (13) or with the  $24p$  frequencies corresponding to them should be equal to zero.

The force constants  $k$ 's are not all entirely independent. For a small translation of the entire crystal specified by  $\mathbf{u} = (u_1, u_2, u_3)$ , we get from (4) that  $\sum_{j, \rho, \sigma} u_j k_{irs}^{j\rho\sigma} = 0$  ( $\sigma = 1$ , to  $2N + 1$ ).

Since this relation is true for any arbitrary vector  $\mathbf{u}$ , we get

$$\sum_{\rho, \sigma} k_{irs}^{1\rho\sigma} = \sum_{\rho, \sigma} k_{irs}^{2\rho\sigma} = \sum_{\rho, \sigma} k_{irs}^{3\rho\sigma} = 0. \quad (15)$$

We shall now consider in greater detail the behaviour of  $\frac{d\omega}{da}$  at the point  $\theta_1 = \theta_2 = \theta_3 = 0$ . By adding the elements of the columns  $3s + i$  ( $i = 1, 2, 3$ ;  $s = 1, 2, \dots, p$ ) respectively to the corresponding elements of the first, second and third columns, we can easily see with the aid of the relations (15) that  $\omega^6$  is a factor of  $|A - M\omega^2|$ .

∴ Three of the frequencies corresponding to zero values of  $\theta_1$ ,  $\theta_2$  and  $\theta_3$  are zero and also the expression  $\frac{d\omega}{da} = U(a)$  tends to a definite value  $(-s_{3p}''(0)/2s_{3p-1}(0))^{1/2}$  for these three frequency branches. Hence subtracting these three modes which correspond to a translation of the entire crystal, one can see that the group velocity of the waves associated with each of the  $(24p-3)$  characteristic frequencies is equal to zero.

### 3. THE EFFECT OF AN INITIAL DISTURBANCE

We consider here the nature of the propagation of an initial disturbance confined to a small region into the entire crystal and the state of movements of the atoms about their equilibrium positions at a later instant. Any such disturbance will set out a train of progressive waves in the medium and physically it is easy to see that wave clusters having zero group velocity alone could have any significant influence over the vibrations of the atoms near the source of disturbance at a subsequent instant. In this section, it is shown that there is such a tendency on the part of the disturbance agitating the atoms to resolve itself gradually into a set of harmonic vibrations, with exactly the same frequencies as of these wave clusters and that the contributions to the vibrational energy of the atoms due to all other frequencies are insignificant, being second-order quantities. Next, the dependence of the amplitudes of vibrations of the atoms on the factor  $t^{-3/2}$  is interesting and suggests a correlation with thermal conductivity.

We shall suppose that initially all the atoms in the cell with index zero  $(0, 0, 0)$  of the lattice are displaced by small amounts and that the velocities of all the atoms are zero. In other words, the initial state of movements of the atoms is described by

$$q_{irs}(0) = \frac{1}{8\pi^3c} \int_{\Delta} u_r^i e^{ia.s} dV = u_r^i \delta_{rs} \quad (16)$$

$$\text{and } \dot{q}_{irs}(0) = 0, \quad (17)$$

where  $dV = da_1 da_2 da_3 = cd\theta_1 d\theta_2 d\theta_3$ ,  $(a_1, a_2, a_3)$  being the components of the wave vector in any three orthogonal directions in the reciprocal lattice and  $c$  is the determinant of the transformation  $a_i = \sum_j c_{ij} \theta_j$  ( $i, j = 1, 2, 3$ );  $\Delta$  denotes the volume enclosed by the parallelepiped whose corners are given by  $\pi(\pm \mathbf{b}_1 \pm \mathbf{b}_2 \pm \mathbf{b}_3)$ .

At any subsequent instant, the displacements of the atoms from their equilibrium positions can be obtained by the superposition of the waves of the type (5) and we have

$$q_{irs}(t) = \frac{1}{16\pi^3c} \sum_{k=1}^{3p} \int_{\Delta} A_{r,k}^i (e^{i\omega_k t} + e^{-i\omega_k t}) e^{iu.s} dV \quad (18)$$

where  $A_{r,k}^i$  denotes the amplitude  $A_r^i$  of the  $r$ th particle in any cell in the direction  $x^i$  corresponding to the frequency branch  $\omega_k$  of (10) and we should further have

$$\sum_{k=1}^{3p} A_{r,k}^i = u_r^i \tag{19}$$

to be in conformity with the initial conditions (16, 17).

A discussion of the variation of the above integral with time is not in general possible, as it requires a knowledge of the force constants and the actual expressions for the frequency branches; however the analogy of a linear lattice shows that no particle can acquire a sensible amplitude until the fastest group corresponding to the elastic waves reaches that lattice point. We obtain here an asymptotic approximation of (18), which describes the nature of the movements of the atoms a long time after the initial disturbance.

We shall denote the eight saddle points (13) at which  $\frac{d\omega}{da} = 0$  by  $\mathbf{a}^\alpha = (a_1^\alpha, a_2^\alpha, a_3^\alpha)$  ( $\alpha = 1, 2, \dots, 8$ ) and the corresponding value of  $\omega_k$  by  $\nu_k^\alpha$  ( $k = 1, 2, \dots, 3p$ ). For  $\mathbf{a}^1 = (0, 0, 0)$ , three of the frequencies of (10) are zero and these frequencies may be denoted by  $\nu_1^1 = \nu_2^1 = \nu_3^1 = 0$ . Further, let  $\Delta_k = |b_{rs}|$  where  $|b_{rs}|$  is the determinant of order three whose elements are given by  $b_{rs} = b_{sr} = \frac{\partial^2 \omega_k}{\partial a_r \partial a_s}$  and let the values of  $\Delta_k$  and  $A_{r,k}^i$  which are functions of  $\mathbf{a}$  at the eight saddle points be denoted by  $\Delta_k^\alpha$  and  $A_{r,k}^{i\alpha}$ . Then from the result proved in the Appendix, we get the following expression for the asymptotic value of  $q_{irs}(t)$ .

$$q_{irs}(t) = \frac{1}{c(2\pi t)^{3/2}} \sum_{k=1}^{3p} \frac{A_{r,k}^{i,1}}{|\Delta_k^1|^{1/2}} \cos \left( \nu_k^1 t + k^1 \frac{\pi}{4} \right) + \frac{1}{c(2\pi t)^{3/2}} \sum_{\alpha=2}^8 \sum_{k=1}^{3p} \frac{A_{r,k}^{i,\alpha}}{|\Delta_k^\alpha|^{1/2}} \cos \left( \nu_k^\alpha t + \mathbf{a}^\alpha \cdot \mathbf{s} + k^r \frac{\pi}{4} \right) \tag{20}$$

( $i = 1, 2, 3; r = 1, 2, \dots, p$ )

here  $k^\alpha$  is the signature of the matrix of the determinant  $\Delta_k^\alpha$ .

An equation analogous to (20) can be derived by an exactly similar procedure if initially a group of atoms in any cell have small velocities, but no displacements. When this is done, the general expressions for the vibrations of the atoms about their mean positions under any initial condition regarding their velocities and displacements are easily obtained by the principle of superposition. In any case, *the state of movements of the atoms tends asymptotically to a superposition of the (24 p-3) characteristic vibrations of the crystal, with amplitudes that vary inversely as  $t^{3/2}$ .*



These vibrations were first predicted and described by Sir C. V. Raman. The  $(3p-3)$  modes contained in the first summation can be pictured as the oscillations with respect to each other of the  $p$  interpenetrating Bravais lattices of atom of which the crystal is built up, while since  $\mathbf{a}^{\alpha} \cdot \mathbf{s}$  is an integral multiple of  $\pi$ , the remaining  $21p$  modes represent the oscillations of the alternate layers of equivalent atoms against each other. The number of the distinct characteristic frequencies might be considerably reduced for crystals exhibiting a high degree of symmetry. It is worthy of note that the  $21p$  modes have the same status as the remaining  $(3p-3)$  modes as far as the dynamical behaviour of the system is concerned, though it is the latter that are active in the first order Raman effect; their importance arises in the second order Raman effect in crystals, where they exhibit themselves as combinations and overtones of the fundamental frequencies.

I am very much indebted to Professor Sir C. V. Raman, N.L., for his encouragement and suggestions, during the course of this work.

#### SUMMARY

It has been shown that the structure of a crystal as a three-dimensional repetitive pattern of lattice cells of atoms leads automatically to the result that the group velocity of the waves associated with the  $(24p-3)$  characteristic frequencies should be equal to zero, and hence that oscillations having these frequencies are in the nature of stationary normal modes of vibration of the crystal lattice. It has further been proved that any arbitrary initial disturbance asymptotically settles into a superposition of these  $(24p-3)$  characteristic vibrations which were first predicted by Raman, and that their amplitudes of vibration vary inversely as  $t^{3/2}$  and further, that the energies associated with other frequencies of vibration are of negligible magnitude.

#### APPENDIX

Consider the integral  $I = \int_D f(x) \exp. i [\omega(x)t - k \cdot x] dV,$  (1)

where  $x=(x_1, x_2, x_3)$  and  $k=(k_1, k_2, k_3)$  and  $dV = dx_1 dx_2 dx_3$ . We shall assume that  $f(x)$  is integrable in  $D$  and that the region of integration contains only one stationary point of  $\omega(x)$  at  $x = x_0 = (x_{10}, x_{20}, x_{30})$ . When  $t$  is large enough as to make  $\exp. i\omega(x)t$  a very rapidly fluctuating function compared to  $f(x) \exp. ik \cdot x$ , an approximation to the above integral can be effected by the application of the principle of stationary phases due to Kelvin. A fairly good estimate of (1) can be obtained if  $Mt = 0$  ( $|k|^2$ ), where  $M$  is a constant of the dimensions of distance, for in this case  $\omega(x)t$  is a second order quantity compared to  $k \cdot x$ . The principle of Kelvin states that the maximum contribution to an integral containing a very rapidly fluctuating

function arises only from the regions in the neighbourhood of points at which the function is stationary. A rigorous justification of this principle for integrals involving one variable was given by Watson<sup>5</sup>; a formal extension of it to integrals of the type (18) involving three variables is given below.

If we write  $(x_i - x_{i0}) = \xi_i$  ( $i = 1, 2, 3$ ), for small values of  $\xi_1, \xi_2, \xi_3$ , we have by Taylor's theorem

$$\omega(x) = \omega(x_0) + \frac{1}{2} \sum_{r,s} a_{rs} \xi_r \xi_s \tag{2}$$

where  $a_{rs} = a_{sr} = \left( \frac{\partial^2 \omega}{\partial x_r \partial x_s} \right)_{x=x_0}$

Hence an approximation for (1) would be  $I \sim f(x_0) e^{i[\omega(x_0)t - k \cdot x_0]}$

$$\int_{D_1} e^{\frac{it}{2} \sum_{r,s} a_{rs} \xi_r \xi_s} d\xi_1 d\xi_2 d\xi_3 \tag{3}$$

$D_1$  being any small region completely enclosing the point  $x_0$ .

If we transform the variables  $\xi_1, \xi_2, \xi_3$  to a new set of variables  $\eta_1, \eta_2, \eta_3$  so that the new co-ordinate axes coincide with the directions of the principal diameters of the quadric  $\sum_{r,s} a_{rs} \xi_r \xi_s = 1$  in the  $\xi$  space, then

$$\sum_{r,s} a_{rs} \xi_r \xi_s = \lambda_1 \eta_1^2 + \lambda_2 \eta_2^2 + \lambda_3 \eta_3^2, \tag{4}$$

$\lambda_1, \lambda_2, \lambda_3$  being the eigenvalues of the matrix  $(a_{rs}) = A$ . Since  $(a_{rs})$  is symmetric, the roots of  $|A - \lambda I| = 0$  are real. Also, we have  $d\xi_1 d\xi_2 d\xi_3 = d\eta_1 d\eta_2 d\eta_3$ . Hence (3) becomes

$$I \sim f(x_0) e^{i[\omega(x_0)t - k \cdot x_0]} \int_{D_2} e^{\frac{it}{2} (\lambda_1 \eta_1^2 + \lambda_2 \eta_2^2 + \lambda_3 \eta_3^2)} d\eta_1 d\eta_2 d\eta_3 \tag{5}$$

$D_2$  being the region corresponding to  $D_1$  in the  $\eta$  space.

If therefore  $\lambda_1, \lambda_2, \lambda_3$  are all positive (say) then by writing  $\sqrt{\lambda_r} t \eta_r = y_r$  ( $r = 1, 2, 3$ ), we can take the limits for  $y_1, y_2, y_3$  to be  $-\infty$  to  $+\infty$  as  $t$  is large. Hence (5) becomes

$$I \sim \frac{f(x_0) e^{i[\omega(x_0)t - k \cdot x_0]}}{|\Delta|^{1/2} t^{3/2}} \prod_{r=1}^3 \int_{-\infty}^{+\infty} e^{-y_r^2/2t} dy_r \tag{6}$$

$$(r = 1, 2, 3), \text{ Lt } t \rightarrow \infty$$

$$= \left( \frac{2\pi}{t} \right)^{3/2} \frac{f(x_0)}{|\Delta|^{1/2}} e^{i[\omega(x_0)t - k \cdot x_0 + 3\pi/4]}$$

for from (4),  $\lambda_1 \lambda_2 \lambda_3 = \Delta$ , the determinant of the matrix A,

In general we have

$$I = \left(\frac{2\pi}{t}\right)^{3/2} \frac{f(x_0)}{|\Delta|^{1/2}} \exp i [\omega(x_0)t - k \cdot x_0 + s\pi/4] \text{ Lt } t \rightarrow \infty \quad (7)$$

where  $s$  is the *signature of the matrix* (A), i.e., the difference between the number of positive eigenvalues to the number of negative eigenvalues of the matrix A.

Similarly the value of the integral

$$I' = \int_D f(x) \exp i (-\omega(x)t + k \cdot x) dV, \text{ is given by}$$

$$I' = \left(\frac{2\pi}{t}\right)^{3/2} \frac{f(x_0)}{|\Delta|^{1/2}} \exp i [-\omega(x_0)t + k \cdot x_0 - s\pi/4] \quad (8)$$

When the region of integration contains several stationary points, it can be split up into subregions in each of which the function has only one stationary point and the final result simply consists of the sums of terms like (7).

#### REFERENCES

1. Born, Max .. *Atom theories Das Festen Zustandes Teubner, Leipzig, 1923.*
2. Blackman, M. .. *Proc. Roy. Soc., 1935, 148 A, 390.*
3. Raman, C. V. .. *Proc. Ind. Acad. Sci., 1943, 18 A, 237.*
4. ————— .. *Ibid., 1947, 26, 339.*
5. Watson, G. N. .. *Proc. Camb. Phil. Soc., 1918, 19, 49.*