*Reprinted from "The Proceedings of the Indian Academy of Sciences", Vol. XXXVII, No. 3, Sec. A, 1953*

# THE CHARACTERISTIC VIBRATIONS OF CRYSTAL LATTICES—PART II

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Received March 9, 1953
(Communicated by Sir C. V. Raman, N.L.)

## 1. Introductory Remarks

The transference of a particular state from one part of a medium to another, without any bodily movement of the medium itself, is well known as *wave motion* in a material substance. For a discrete structure, such as a crystal, the disturbance arising from a wave progressing through the medium is defined only at the set of lattice points which are the mean positions of the atoms of the crystal. Wave propagation in crystal lattices should further be consistent with the constraints imposed by the dynamical equations of motion of the system and this in general makes the waves dispersive. By assuming waves through atoms of the same type in the crystal architecture, it was shown in a preceding paper that there are $(24p - 3)$ frequencies for the system which have the remarkable property of making the group velocity of the waves associated with them, equal to zero. These frequencies, in their turn, correspond to eight wave vectors in the reciprocal lattice.

To assign the direction of propagation of these eight types of wave fronts, we first note that an equation of the form $\eta = r \cos(\omega t - \mathbf{a}.\mathbf{s})$ denotes a wave front progressing in the direction of the vector $\mathbf{a}$ and that at any instant, the displacement is a constant for all points on the plane $\mathbf{a}.\mathbf{s} =$ constant. The vector $(0, 0, \pi)$ now indicates the direction $\mathbf{b}_3$ of the reciprocal lattice and thus at any instant the displacements arising out of a plane wave of this wave-vector should be the same for all the atoms in a plane defined by the $\mathbf{d}_1$, $\mathbf{d}_2$ axes of the crystal. This vector, in effect, denotes modes in which alternate such layers of the crystal vibrate with opposite phases at any instant and with the same amplitudes. As the displacements of a wave in a crystal are defined only at its lattice points, the concept of a wave motion here ceases to have meaning except in a formal sense and the $3p$ modes associated with this vector are strictly stationary modes of vibrations; and a similar argument applies to each of the $(24p - 3)$ modes mentioned above. Again, three of the frequency branches $\omega_k$ $(k = 1, 2, 3)$ of the secular equation

(I, 8) tend to zero with $\mathbf{a}$ and as $\underset{a\to 0}{\mathrm{Lt}} \frac{\omega_k}{a} = \frac{d\omega_k}{da}$, we get the interesting result that the group and wave velocities of the elastic waves are identical.

It was further shown in Part I that any arbitrary initial disturbance inside the crystal tends asymptotically to a superposition of these characteristic vibrations. The object of the present paper is to discuss the reduction of the distinct number of terms of the asymptotic expression in the case of degeneracy in these modes and to consider some interesting corollaries resulting from it.

## 2. DEGENERACY

We adopt throughout the notation of Part I, except with slight modifications. Writing $\mathbf{q}_{rs} = (q_{1rs}, q_{2rs}, q_{3rs})$; $\mathbf{A}_r = (\mathrm{A}_r{}^1, \mathrm{A}_r{}^2, \mathrm{A}_r{}^3)$ and $\mathbf{A}_r(\mathbf{a}^\alpha) = \mathbf{A}_r(\alpha)$, the asymptotic expression (I, 20) for the displacements of the atoms from their equilibrium positions becomes

$$\mathbf{q}_{rs} = \frac{1}{c\,(2\pi t)^{3/2}} \sum_{k=4}^{3p} \frac{\mathbf{A}_{r,k}{}^{(1)}}{|\Delta_k{}^1|^{\frac{1}{2}}} \cos\,(v_k{}^1 t + k^1 \pi/4)$$

$$+ \frac{1}{c\,(2\pi t)^{3/2}} \sum_{\alpha=2}^{8} \sum_{k=1}^{3p} \frac{\mathbf{A}_{r,k}{}^{(\alpha)}}{|\Delta_k{}^\alpha|^{\frac{1}{2}}} \cos\,(v_k{}^\alpha t + \mathbf{a}^\alpha \cdot \mathbf{s} + k^\alpha \pi/4) \quad (1)$$

For crystals possessing symmetry, degeneracies may arise and the number of distinct terms contained in (1) could be considerably reduced. It has been shown by E. V. Chelam[1] that if under a symmetry operation of the crystal two vectors $\mathbf{a}^\alpha$ and $\mathbf{a}^{\alpha'}$ go over into each other, the set of $3p$ frequencies associated with each of them are the same for both the vectors. The set of all vectors which are transforms of each other under the symmetry group of the crystal constitutes an *equivalent* set. The $3p$ frequencies associated with all the vectors in an equivalent set are the same and differ only in their order of arrangement. The vector $\mathbf{a}^1 = (0, 0, 0)$ representing the unit element of the translational group forms always a set by itself. A further degeneracy among the $3p$ frequencies associated with any of the eight vectors $(\mathbf{a}^\alpha)$ is also possible depending on the crystal symmetry. We now prove an interesting result that if,

$$v_k{}^\alpha = v_s{}^{\alpha'}, \text{ then } \Delta_k{}^\alpha = \Delta_s{}^{\alpha'}. \quad (2)$$

Differentiating the equation (I, 10)

$$\sum_{t=0}^{3p} s_t\, z^{3p-t} = 0 \quad (3)$$

twice with respect to $a$ and making use of the results $\frac{ds_t}{da} = 0; \frac{d\omega}{da} = 0$ at the eight points $\mathbf{a} = \mathbf{a}^\alpha$ $\left(\frac{d\omega_k}{da} \neq 0 \text{ at } \mathbf{a} = 0 \text{ for } k = 1, 2, 3\right)$, we get

$$2\omega(\alpha)\frac{d^2\omega}{da^2}(\alpha) = -\frac{\sum_{t=1}^{3p}\frac{d^2s_t}{da^2}(\alpha)\, z^{3p-t}(\alpha)}{\sum_{t=0}^{3p-1} s_t(\alpha)(3p-t)\, z^{3p-t-1}(\alpha)}. \tag{4}$$

Here functions of the vector $\mathbf{a}^\alpha$ are denoted simply by its suffix $\alpha$ in the argument, for example $s_t(\mathbf{a}^\alpha) = s_t(\alpha)$. It is obvious from (4) that if $\omega_k(\alpha) = \omega_s(\alpha)$, then $\frac{d^2\omega_k}{da^2}(\alpha) = \frac{d^2\omega_s}{da^2}(\alpha)$, the numerators and denominators in both the functions being equal to each other. For the case $\omega_k(\alpha) = \omega_s(\alpha')$, if we could prove that $\frac{d^2s_t}{da^2}(\alpha) = \frac{d^2s_t}{da^2}(\alpha')$, then from (4) it would follow that $\frac{d^2\omega_k}{da^2}(\alpha) = \frac{d^2\omega_s}{da^2}(\alpha')$.

To show this result, we note that the coefficients $s_t$ $(t = 1, 2 \ldots . 3p)$ are symmetric functions of the roots of (3) and hence are *invariants* for all the vectors of an equivalent set. Thus, if $\mathbf{a}^\alpha$ and $\mathbf{a}^{\alpha'}$ are two vectors belonging to an equivalent set, then

$$s_t(\alpha) = s_t(\alpha') \qquad (t = 1, 2 \ldots . 3p) \tag{5}$$

Now the coefficients $s_1, s_2 \cdots s_{3p}$ of the various powers of $z$ in (3) can be considered to be the components of a vector $\mathbf{s}$ in a $3p$-dimensional space N. This process sets a homomorphism between the vectors of the reciprocal space R and the corresponding vectors $\mathbf{s} = (s_1, s_2 \cdots s_{3p})$ in N; all equivalent vectors in R map the same vector in N. Starting from a vector $\mathbf{s}(\rho)$ in N, another one whose components are the derivatives $\frac{ds_i}{da}$ *at the point* $\mathbf{a} = \mathbf{a}^\rho$ of $s_i$ could be obtained by means of the operator D, *i.e.*, $\mathbf{Ds}(\rho) = \frac{d\mathbf{s}}{da}(\rho)$. To a linear transformation $t: \mathbf{a} \to \mathbf{a}' = t\mathbf{a}$ in R corresponds in N the transformation T: $\mathbf{Ts}(\mathbf{a}) = \mathbf{s}(\mathbf{a}')$. All linear correspondences in R which transform into themselves the vectors of an equivalent set, go over into the identity matrix I in R, in view of the relations (5). If $\mathbf{a}^\alpha$ and $\mathbf{a}^{\alpha'}$ are two vectors of an equivalent set in R such that $\mathbf{a}^{\alpha'} = t'\mathbf{a}^\alpha$, this correspondence in N is given by $\mathbf{s}(\alpha') = \mathbf{Is}(\alpha) = \mathbf{s}(\alpha)$. (6)

As the identity matrix commutes with all matrices in N, we have now

$$\mathbf{D}^2\mathbf{s}(\alpha') = \mathbf{D}^2\mathbf{Is}(\alpha) = \mathbf{ID}^2\mathbf{s}(\alpha) = \mathbf{D}^2\mathbf{s}(\alpha)$$

so that we get

$$\frac{d^2\mathbf{s}}{da^2}(\alpha') = \frac{d^2\mathbf{s}}{da^2}(\alpha).$$

Thus, if $\omega_k(\alpha) = \omega_s(\alpha')$, we get from (4)

$$\frac{d^2\omega_k}{da^2}(\alpha) = \frac{d^2\omega_s}{da^2}(\alpha'). \tag{7}$$

In a similar way we could show that

$$\frac{\partial^2\omega_k}{\partial a_i \partial a_j}(\alpha) = \frac{\partial^2\omega_s}{\partial a_i \partial a_j}(\alpha') \tag{7 a}$$

and from this, result (2) follows.

Let now the distinct frequencies in (1) be denoted by $c_1, c_2 \ldots c_\rho$. Then if $\nu_k^\alpha = \nu_s^{\alpha'} = c_r$, we can write $\Delta_k^\alpha = \Delta_s^{\alpha'} = \Delta_r$ and $k^\alpha = k_r$. The equation (1) now reduces to the form

$$\mathbf{q}_{rs}(t) = \frac{1}{c(2\pi t)^{3/2}} \sum_{r=1}^{\rho} \frac{\cos(c_r t + k_r \pi/4)}{|\Delta_r|^{\frac{1}{2}}} \left( \sum_{\alpha, k} \mathbf{A}_{r,k} \cos \mathbf{a}^\alpha \cdot \mathbf{s} \right) \tag{8}$$

the summation inside the brackets being over all values of $\alpha$ and $k$ such that $\nu_k^\alpha = c_r$.

## 3. Effect of a Translation

We shall suppose that initially all the cells of the crystal bounded by the parallelopiped (D) whose edges are $l_1\mathbf{d}_1$, $l_2\mathbf{d}_2$, $l_3\mathbf{d}_3$ undergo a small translation specified by the vector $\mathbf{u} = (u_1, u_2, u_3)$. Then the initial conditions are described by

$$\mathbf{q}_{rs}(0) = \frac{\mathbf{u}}{8\pi^3 c} \int_\Delta \sum_\sigma e^{i\alpha\cdot(s-\sigma)}\, dV \tag{9}$$

the summation extending over all the cells contained in D and $\dot{\mathbf{q}}_{rs}(0) = 0$.

At a later instant, the displacements of the atoms about their equilibrium positions are given by

$$\mathbf{q}_{rs}(t) = \frac{1}{16\pi^3 c} \sum_{k=1}^{3p} \int_\Delta \mathbf{A}_{r,k} (e^{i\omega_k t} + e^{-i\omega_k t}) \left( \sum_\sigma e^{i\alpha\cdot(s-\sigma)} \right) dV \tag{10}$$

where we have from the initial conditions (9) the following relation

$$\sum_{k=1}^{3p} \mathbf{A}_{r,k} = \mathbf{u}. \tag{11}$$

If we write $\mathbf{A}_{r,k}\,(\sum_{\sigma} e^{-ia\cdot\sigma}) = \mathbf{B}_{r,k}$, then the asymptotic value of (10) is given by

$$\mathbf{q}_{rs}(t) = \frac{1}{c\,(2\pi t)^{3/2}} \sum_{k=4}^{3p} \frac{\mathbf{B}_{r,k}^{(1)}}{|\Delta_k^1|^{\frac{1}{2}}} \cos\,(v_k^1 t + k^1\pi/4)$$

$$+ \frac{1}{c\,(2\pi t)^{3/2}} \sum_{\alpha=2}^{8} \sum_{k=1}^{3p} \frac{\mathbf{B}_{r,k}^{(\alpha)}}{|\Delta_k^\alpha|^{\frac{1}{2}}} \cos\,(v_k^\alpha t + \mathbf{a}^\alpha\cdot\mathbf{s} + k^\alpha\pi/4) \quad (12)$$

Now

$$e^{-ia\cdot\sigma} = \sum_{\sigma} e^{-i(\sigma_1\theta_1+\sigma_2\theta_2+\sigma_3\theta_3)}$$

$$= \prod_{r=1}^{3} \frac{(1 - e^{-il_r\theta_r})}{(1 - e^{-i\theta_r})}$$

so that

$$\mathbf{B}_{r,k}^{(\alpha)} = \mathbf{A}_{r,k}^{(\alpha)} \prod_{r=1}^{3} \frac{(1 - e^{-il_r\theta_r})}{(1 - e^{-i\theta_r})}, \quad (13)$$

where the $\theta$'s have any one of the values 0 or $\pi$.

If $l_1$, $l_2$, $l_3$ are all even *or* if the region that undergoes a translation contains an integral number of supercells of the lattice, then

$$\mathbf{B}_{r,k}^{(\alpha)} = 0 \text{ from (13)} \qquad (\text{for } \alpha = 2,\ 3\cdots 8),$$

so that the asymptotic state of movements of the atoms consists only of the $(3p - 3)$ modes of vibrations in which equivalent atoms in successive cells vibrate with the same phases and amplitudes. If two of these numbers are even and the other odd (say, $l_1$ and $l_2$ are even and $l_3$ is odd), then $\mathbf{B}_{r,k}^{(\alpha)} = 0$ for the set of points $(0, \pi, \pi)$; $(\pi, 0, 0)$; $(\pi, 0, \pi)$; $(\pi, \pi, 0)$ and $(\pi, \pi, \pi)$. At the point $(0, 0, \pi)$, $\mathbf{B}_{r,k}^{(\alpha)} = l_1 l_2\,\mathbf{A}_{r,k}^{(\alpha)} \neq 0$. Thus in this case, in addition to the $(3p - 3)$ modes, the state of vibrations of the atoms of the crystal consists of $3p$ other modes in which equivalent atoms in consecutive cells along the direction of the axis $d_3$ vibrate with opposite phases. Similarly, when the region undergoing the translation contains an even number of cells along only one of the axes of the crystal, it can be seen that the amplitudes of $12p$ vibrations are equal to zero and when $l_1$, $l_2$, $l_3$ are all odd, all the $(24p - 3)$ modes will be active.

It should be mentioned that the above statements are true only to a first order of approximation, as we have in deriving (1) neglected infinitesimals of order higher than $t^{-3/2}$. We note that a translation of an unit cell of the crystal results in exciting all the $(24p - 3)$ vibrations. The same translation applied to an adjacent cell along one of the crystal axes causes displacements in which the amplitudes of the vibrations of the planes intersecting this axis

against each other, occur with opposite signs to the corresponding vibrations excited by its neighbour. The physical explanation of the above results now follows from the fact that in any bodily movement of two adjacent cells, such vibrations annul each other leaving only $(12p - 3)$ vibrations intact. By the same reasoning, we can show that an initial disturbance consisting of translations by the same amount, but in opposite directions of two supercells excites none of these vibrations and the displacements of any atom arising out of such a disturbance tends asymptotically to zero. Applied to an actual crystal, say the diamond[2] in which degeneracies are present, these results show that a translation of one of its supercells excites only the 1332 vibration, while in a disturbance arising out of a translation of an unit consisting of an even number of cells along only one of its axes, all the eight distinct modes of oscillation of the crystal will be active.

The author's grateful thanks are due to Professor Sir C. V. Raman for suggesting the problem and for his guidance during the course of this work.

## SUMMARY

It is shown that the wave and group velocities of the elastic waves are identical. An initial disturbance consisting of a translation of a supercell excites asymptotically the $(3p - 3)$ characteristic vibrations only, the amplitudes of the remaining $21p$ modes being zero to a first order of approximation. A translation of a single unit cell results in exciting all the $(24p - 3)$ modes of vibrations of the crystal. The question of reduction of the asymptotic expression for the displacements of the atoms about their mean positions to its simplest form, when degeneracies are present in these vibrations, is also considered.

## REFERENCES

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