THE NATURE OF THE THERMAL AGITATION IN CRYSTALS

BY SIR C. V. RAMAN

(Memoir No. 77 of the Raman Research Institute, Bangalore 6)

Received October 8, 1955

1. INTRODUCTION

The present memoir concerns itself with a problem of fundamental importance in the physics of the solid state, namely the determination of the nature of the atomic movements which constitute the thermal agitation in a crystal. It would be no exaggeration to say that on our taking the correct view of the nature of these movements depends the possibility of our understanding the physical behaviour of crystals aright, not only in the thermal field but also in diverse other fields, as for example their spectroscopic behaviour and the phenomena of X-ray diffraction in crystals. The problem is considered in this paper from two distinct points of view. The first method of approach is to examine the basic experimental facts in the light of fundamental physical principles and to draw the inferences following logically therefrom. The second method of approach is the analytical investigation of the problem on the basis of classical mechanics and the general principles of thermodynamics and the quantum theory. The result in either case is to show that the ideas underlying the well-known specific heat theory of Debye and the lattice dynamics of Born and his collaborators are untenable. The picture of the thermal agitation in a crystal which emerges from the present investigation is fundamentally different from that postulated in the theories of Debye and Born.

2. SOME GENERAL CONSIDERATIONS

The identification on a quantitative basis of the thermal energy of a crystal with the energy of atomic oscillations rests on two fundamental ideas; (a) that the oscillators can be enumerated, their total number being three times the number of atoms comprised in the crystal; (b) that the energy of the oscillators is quantized and for any particular frequency has an average value which can be calculated with the aid of Boltzmann’s theorem. We proceed to examine these ideas critically with a view to determine their precise significance as well as their implications.

The first of the two ideas referred to above is based on the fundamental theorem in classical mechanics which states that all the possible modes of
small vibration of a system of connected particles are superpositions of a set of normal modes, the number of such modes being the same as the number of degrees of dynamic freedom of the system, and further that in each such normal mode all the particles of the system have the same frequency of vibration and oscillate in the same or opposite phases. In the present context, therefore, the term oscillator must be considered as referring to a set of atoms vibrating in a normal mode, all of them having the same frequency and the same or opposite phases of vibration.

The second idea, namely that of averaging the energy of an oscillator, arises because of the chaotic nature of thermal agitation which involves energy fluctuations whose magnitude is determined by the frequency of the vibration. The theorem of Boltzmann which enables the average to be calculated is a description in statistical form of the behaviour of the individual units in an assembly consisting of an immense number of such units which are physically identical but differ in their energy states and being in a position to exchange energy with each other form a system in thermodynamic equilibrium. In the present context, the units are the oscillators defined in the preceding paragraph. Hence, if the application of Boltzmann's theorem is to be legitimate, it is necessary to postulate that in the crystal is present an assembly of this nature, viz., a great number of individual oscillators all of which vibrate with the same frequency but are in the different energy states permitted by the quantum theory. For each separate frequency of oscillation, a fresh assembly of that nature is needed to enable the energy for each individual frequency to be separately averaged.

The foregoing theoretical picture of the thermal agitation agrees completely with the actual physical picture in the case under consideration. For, every crystal is itself an assembly of an immense number of similar and similarly situated groups of atoms, the internal vibrations of which can occur with one or another of the characteristic frequencies of the group. The energy of vibration of a group with any one of these frequencies may have any of the series of values allowed by the quantum theory and hence would vary from group to group in an entirely unpredictable manner within the crystal. Such a picture would be in perfect harmony with the basic notions of thermodynamics, but would be wholly irreconcilable with any theory which seeks to identify the energy of thermal agitation with the energy of regular wave propagation in the crystal. But this latter idea is precisely what forms the basis of the specific heat theories of Debye and Max Born. It follows that these theories are fundamentally misconceived and must therefore fail, together with all their consequences.
The Nature of the Thermal Agitation in Crystals

3. The Normal Modes of Vibration

The normal modes of vibration of the atomic groupings in the crystal referred to above may be determined and enumerated without any difficulty. It is obviously not permissible in this connection to regard the unit cell in the crystal structure as isolated from the rest of the crystal. For, any oscillation which occurs in a particular cell will necessarily communicate itself immediately to the surrounding cells and set the latter in vibration with the same frequency. Hence, to ascertain the normal modes of vibration, we have to consider vibrations extending over domains whose dimensions are at least as large as the range of the inter-atomic forces. Further, to ensure that the oscillations persist unchanged in character, it is necessary to assume that the oscillation in each of the unit cells included within such a domain is similar and similarly related to the oscillations in the cells surrounding it.

Remembering that in a normal mode the oscillations of all the particles have the same frequency and the same or opposite phase, the foregoing requirements lead us to the following description of the normal modes of vibration: In any normal mode, the oscillations of equivalent atoms in adjoining cells have the same amplitude of vibration but their phases are either the same or the opposite in the cells adjacent to one another along one, two or all three of the axes of the lattice structure. Thus there are $2 \times 2 \times 2$ or 8 possible situations. As a consequence of the identity of the amplitudes of vibration of equivalent atoms in all the cells which need to be considered, the $3p$ equations of motion of the $p$ atoms in any particular cell contain only $3p$ unknowns. Accordingly, it becomes possible to solve the equations completely and determine the $3p$ normal modes and the corresponding frequencies of vibration. As there are eight different situations in respect of the phases of vibration, the equations of motion would necessarily be different in each of them. Accordingly we have $3p \times 8$ or $24p$ normal modes and frequencies of vibration.

An alternative and convenient way of describing the normal modes is to consider a supercell of the lattice whose dimensions are twice as large in each direction as the unit cell. Such a supercell would contain $8p$ atoms and the total number of degrees of freedom associated therewith would be $24p$, and this is the same as the number of normal modes permissible. We may therefore describe these modes as the vibrations of the atoms comprised in the supercell. When this description is adopted, it becomes immediately evident that three of these modes would represent simple translations of the supercell and would therefore have to be excluded in enumerating the internal vibrations of the supercell. We have then left only $(24p - 3)$ normal modes of vibration properly so-called.
4. WAVE PROPAGATION IN CRYSTAL LATTICES

As is well known, the classical theory of elasticity leads to the conclusion that three types of waves can be propagated in any given direction within crystal with the velocities determined by the density of the material and certain linear combinations of its elastic constants. The analysis which leads to this result regards the volume elements of the crystal as simple mass particles whose equations of motion can be written down in terms of the tractive forces arising from the elastic strains. Hence the theory and its consequences would cease to be applicable when these assumptions are invalid and the position would then have to be considered afresh from the atomistic standpoint. A formal investigation on the latter basis shows that only in the limiting case of very low frequencies and of correspondingly long waves are the results of the classical theory of elasticity valid. When we enter the region of the higher frequencies, the phase velocity and the group velocity diverge from each other and the very significant result emerges that the group velocity vanishes for $(24p - 3)$ modes of vibration of the lattice. These modes are found to be identical with the $(24p - 3)$ normal modes referred to in the foregoing section.

To avoid breaking the thread of the argument, the detailed dynamical investigation which has been worked out by Dr. K. S. Viswanathan is printed as an appendix to this memoir. It will therefore suffice here to comment on the significance of the results there derived by him. As is very well understood, it is the group velocity which is physically significant in all considerations regarding wave-propagation, since it is a measure of the rate of energy transport in the medium. The vanishing of the group velocity for the whole series of characteristic frequencies of atomic vibration signifies that there is no wave propagation in the real or physical sense of the term when we are considering oscillations in which the interatomic displacements play a significant role. It follows that considerations of the kind used in the classical theory of elasticity to ascertain the normal modes of vibration of a solid body of finite extension are entirely out of place in the atomistic problem. But it is precisely such considerations that are employed in the theories of Debye and Born to describe and enumerate the movements which they identify with the thermal agitation. Thus, even on the basis of the classical mechanics, the ideas underlying those theories are unsustainable and they have therefore to be laid aside as being completely unreal.

5. THE FREQUENCY SPECTRUM OF THE THERMAL AGITATION

We may sum up what has been said in the foregoing pages by the statement that the energy of the thermal agitation in a crystal may be identified
The Nature of the Thermal Agitation in Crystals

with the energy of an immense number of atomic oscillators which together fill up the volume of the crystal, the individual oscillators being in the various states of excitation corresponding to each of the \((24 p - 3)\) frequencies common to them all, supplemented by the energy of the low frequency oscillations which the three omitted degrees of freedom represent. These \((24 p - 3)\) frequencies correspond to modes of vibration which are related to the structure of the crystal in precisely definable terms. It will be seen that this description of the thermal agitation bears no resemblance whatever to that envisaged in the theories of Debye and Born; these authors identify the energy of the thermal agitation with the energy of waves in immense numbers traversing the crystal in all directions and having frequencies which are all different from one another, the energy of the wave of any particular frequency as well as the sum total of the energy of all the waves taken together being distributed uniformly over the volume of the crystal.

It is noteworthy that in his fundamental paper of 1907 introducing the quantum theory of specific heats, Einstein derived his expression for the average energy of an oscillator of given frequency assuming, as is indeed necessary for applying Boltzmann's theorem, that the crystal is an assembly of an immense number of oscillators all having the same frequency but in different energy states and in thermodynamic equilibrium with each other. The theories of Debye and Born make use of Einstein's expression for the average energy of an oscillator, while on the other hand the frequencies of the waves with which they identify the thermal agitation are all different from each other. Thus it will be seen that there is no logical consistency in their approach to the specific heat problem. Further, the uniform distribution of the thermal energy through the whole volume of the crystal which such identification demands is irreconcilable with the fundamental ideas regarding the nature of the thermal energy of material bodies inherent in the Second Law of Thermodynamics, namely, that the distribution of the energy over the volume of the crystal should exhibit fluctuations which are the more violent the higher the frequency of vibration.

The foregoing comments do not by any means traverse all the arguments and assumptions on which the theories of Debye and Born are based. One of the basic objections to their method of approaching the specific heat problem is that since wave motions involve progressive changes of phase along the direction of propagation and may have any frequency assigned to them, they can neither be treated as normal modes nor enumerated. The theories of Debye and Born seek to escape this difficulty by postulating that the number of wave motions is identical with the number of degrees of freedom of the system, while the choice of wavelengths is determined by still
another postulate, *e.g.*, the so-called postulate of the cyclic lattice which is claimed to represent the effect of the external boundary of the crystal. Since it is obviously impossible to formulate any boundary conditions for the atomic movements at the external surface of a crystal, the procedure is clearly artificial. But that it is also fallacious becomes evident when we remark that the characteristic modes and frequencies of the atoms in the interior of the crystal are determined exclusively by the structure of the crystal and by the interatomic forces whose range is exceedingly small and hence there exists no justification whatever for the assumption which is inherent in the postulate that these modes and frequencies are influenced by the presence of an external boundary.

6. The Spectroscopic Behaviour of Crystals

It is not proposed in this memoir to discuss how the ideas set forth in it impinge on various aspects of crystal physics. We shall however make a brief reference to those cases in which facts already well established illustrate the validity of the conclusions reached in it.

As Einstein emphasized in his fundamental paper of 1907, the theory of the specific heats of crystals stands in the closest relation to their spectroscopic behaviour. In seeking to explain the data then available for the case of diamond, he made the simplifying assumption that all the oscillators in that crystal have a single common frequency. He recognized however, that in general a crystal would possess several characteristic frequencies and that the expression for its specific heat would involve a summation over them all. In the particular case of diamond, the \((24p-3)\) frequencies indicated by the present theory are reduced from 45 to 9 in number by reason of the cubic symmetry of the crystal. One of these 9 frequencies represents the triply degenerate oscillation of the two lattices of carbon atoms against each other, while the other eight represent either the longitudinal or the transverse oscillations of the layers of carbon atoms in the cubic and octahedral planes of the crystal. In numerous papers published in these *Proceedings* in recent years, it has been shown that all these nine frequencies can be ascertained by spectroscopic observation and that the specific heat of diamond can be successfully evaluated with the aid of the data thus obtained.

But the case of diamond does not stand alone in this respect. In recent years, the spectroscopic behaviour of numerous crystals have been studied by diverse methods, *e.g.*, the scattering of light, absorption in the visible, ultra-violet and infra-red regions of the spectrum, and in particular cases, also their luminescence. The whole of the evidence which has thus come
to hand indicates that the vibration spectrum of a crystal consists of a discrete set of monochromatic frequencies and that where there is any departure from this state of affairs, an adequate explanation is forthcoming.

7. **X-Ray Diffraction in Crystals**

That the atomic vibrations in crystals appear with precisely defined frequencies and with modes bearing a precise geometric relationship to the architecture of the crystal has a most important bearing on the subject of the diffraction of X-rays by crystals. Here again, a particularly striking illustration is furnished by the case of diamond. When a plate of this crystal is traversed by a narrow pencil of X-rays and the resulting Laue pattern is recorded on a photographic plate, it is found that in addition to the usual Laue spots, other sets of sharply defined spots appear on the plate, corresponding to each of the monochromatic components in the incident X-radiation. This phenomenon which was discovered in the year 1940 by Dr. Nilakantan and the present writer using octahedral cleavage plates of diamond has since been thoroughly re-investigated at this Institute by Mr. Jayaraman and the writer. The results are found to be in complete accord with the hypothesis that the incident X-radiation excites the triply degenerate oscillation of the two lattices of carbon atoms in the crystal against each other. These movements occur along the directions of the three cubic axes and as a consequence, all the lattice planes of the crystal are disturbed, giving rise to dynamic X-ray reflections by them. *Three* sharply-defined spots corresponding to each monochromatic component in the incident X-ray beam are demanded by the theory for the dynamic reflections by each of the (111) planes of the crystal, since these planes are equally inclined to the cubic axes. These reflections are actually observed in the directions indicated by the theory with suitable settings of the crystal. Other sets of lattice planes in the crystal also give dynamic reflections in the directions demanded by the theory, but since such planes are unequally inclined to the three cubic axes which are the directions of movement of the atoms in the excited oscillations, they are not all equally conspicuous.

Here again the case of diamond does not stand by itself, since analogous phenomena are also exhibited by other crystals. But it is not necessary here to enter into the details of these cases.

8. **Summary**

The principles of thermodynamics and of the quantum theory indicate that the thermal energy in a crystal is identifiable with the energy of an
immense number of atomic oscillators which have their frequencies of vibration in common but are in different states of excitation. Dynamical investigation of the problem shows that if the crystal contains \( p \) interpenetrating Bravais lattices of atoms, there are \((24p - 3)\) frequencies of vibration common to all the oscillators. An investigation of the propagation of waves in crystal lattices shows that the results of the classical theory of elasticity are valid only in the limiting case of very low frequencies and proves further that the group velocity of the waves vanishes for \((24p - 3)\) frequencies which may accordingly be identified as the characteristic frequencies of atomic vibration in the crystal. Since there is no wave-propagation in the real or physical sense except in the very lowest range of frequencies, the identification of the thermal energy with the energy of waves traversing the crystal in all directions and having frequencies all different from one another which forms the basis of the specific heat theory of Debye and of Born's lattice dynamics ceases to be justifiable. Other aspects of these latter theories are also examined and it is shown that the assumptions which they involve are untenable and that in consequence the theories have no claim to validity. The experimental results which confirm that the atomic oscillators have specific frequencies in common and modes of vibration specifically related to the crystal structure are briefly set out.
We shall consider the most general case of a crystal whose structure includes \( p \) interpenetrating Bravais lattices, all of which are geometrically similar and similarly situated in the crystal arrangement. An unit cell of the crystal will therefore contain \( p \) atoms whose masses we shall denote by \( m_1, m_2, \ldots, m_p \).

Since a crystal is triply periodic in space, any unit cell can be reached from any other cell of the crystal by the application of three primitive translations or integral multiples of them. We denote the three primitive translations by the three vectors \( \mathbf{d}_1, \mathbf{d}_2 \) and \( \mathbf{d}_3 \). In the same way, we denote the three primitive vectors of the reciprocal lattice by \( \mathbf{b}_1, \mathbf{b}_2 \) and \( \mathbf{b}_3 \). In what follows, the symbols \( s \) and \( \sigma \) will be used to denote particular cells in the crystal structure while \( r \) and \( \rho \) will indicate particular atoms in the unit cell; \( X, Y, Z \) are three mutually perpendicular directions chosen as the coordinate axes along which the displacements of the atoms from their equilibrium positions are resolved. We represent the displacement-components of any atom, say the \( r \)th atom in the \( s \)th cell, by means of the symbols \( q_{xrs}, q_{yrs}, q_{zrs} \). We can now write the equations of motion of the atoms in the \( s \)th cell and they take the form

\[
-m_r \ddot{q}_{xrs} = \sum_{\rho \neq s} k_{\rho rs}^x q_{yrs}\quad (x = X, Y, Z) \quad (r = 1, 2, \ldots, p) \quad (1)
\]

The force constant \( k_{\rho rs}^x \) occurring in (1) expresses the proportionality existing between the \( x \)-component of the force acting on the atom \((r, s)\) to the displacement in the \( y \)-direction of the atom \((\rho, \sigma)\) which gives rise to this force.

Since the crystal is composed of \( p \) different Bravais lattices of atoms, we can reasonably expect a wave of a given wavelength and frequency to be propagated with different amplitudes inside the \( p \) different lattices. To solve the set of equations (1), we therefore assume solutions of the form

\[
q_{xrs} = A_{xr} e^{i(\omega t - \mathbf{a} \cdot \mathbf{r})} \quad \left( x = X, Y, Z \right) \quad (r = 1, 2, \ldots, p) \quad (2)
\]

which are plane waves of wavelength \( \lambda \) and circular frequency \( \omega \) propagating in the direction of the vector \( \mathbf{a} \) of the crystal. If we resolve the wave-vector \( \mathbf{a} \) along the three axes of the reciprocal lattice and write \( \mathbf{a} = \theta_1 \mathbf{b}_1 + \theta_2 \mathbf{b}_2 + \theta_3 \mathbf{b}_3 \) then the equations (2) can alternatively be written as

\[
q_{xrs} = A_{xr} e^{i(\omega t - \mathbf{a} \cdot \mathbf{r})} e^{2\pi i \mathbf{r} \cdot \mathbf{a}} \quad (r = 1, 2, \ldots, p) \quad (2')
\]
where \( s_1, s_2 \) and \( s_3 \) are the components of \( s \) along the three Bravais axes of the crystal. Substituting the equations (2) in (1), we obtain

\[
m_{\alpha} \omega^2 \mathbf{A}_{\alpha \beta} = \sum_{\rho_{\beta}} A_{\alpha \rho_{\beta}} \left( \sum_{\sigma_{\beta}} k_{\rho_{\beta} \sigma_{\beta}} e^{i \mathbf{a}_{\beta} \cdot \mathbf{s}} \right) \quad (x = X, Y, Z)
\]

Equations (3) are a set of \( 3p \) equations in the \( 3p \) amplitudes \( A_{x1}, A_{y1}, A_{z1}, A_{x2}, \ldots, A_{zn} \) of the waves. By eliminating the amplitudes from these homogeneous equations, we can obtain a determinantal equation containing \( 3p \) rows and \( 3p \) columns whose elements are the coefficients of the various \( A_{y\rho} \)'s in the equations (3). By expanding this determinant, we can rewrite this equation in the form

\[
S_0 \omega t^p + S_1 \omega t^{p-2} + \ldots + S_{3p} = 0
\]

in which \( S_0, S_1, \ldots, S_{3p} \) are functions of the coefficients of the amplitudes in the equations (3), and hence are also functions of the wave-vector of the waves. The roots of the equations (4) are consequently functions of the wavelengths of the waves, in other words, the waves are dispersive. Since an algebraic equation of degree \( 3p \) has \( 3p \) roots, for each value of \( \alpha \) we obtain \( 3p \) permissible values for \( \omega \) which are the roots of (4). Thus there are \( 3p \) waves of a given wavelength moving in any direction of the crystal.

We shall now consider any one of the \( 3p \) roots of the equation (4). If this is denoted by \( \omega_k \), then \( \omega_k \) expressed as a function of the wave-vector \( \mathbf{a} \) has the following properties:

(i) \( \omega_k \) is a periodic function of \( \theta_1, \theta_2 \) and \( \theta_3 \) with periods \( 2\pi \) for each one of these variables;

(ii) \( \omega_k \) is a real function of \( \theta_1, \theta_2 \) and \( \theta_3 \);

(iii) \( \omega_k \) is an even function of the wave-vector \( \mathbf{a} \) (i.e.), \( \omega_k \mathbf{a} = \omega_k (-\mathbf{a}) \).

Condition (i) follows from the fact that the coefficients of the amplitudes in (3) are of the form

\[
\sum_{\sigma} k_{\rho_{\beta} \sigma_{\beta}} \exp. i\mathbf{a} \cdot (\sigma - s)
\]

and hence are periodic functions of \( \theta_1, \theta_2 \) and \( \theta_3 \) with periods \( 2\pi \) for each of them. The frequencies of the waves which are functions only of these coefficients are therefore also periodic functions of \( \theta_1, \theta_2 \) and \( \theta_3 \).

Condition (ii) can easily be understood from physical considerations. Condition (iii) follows from the fact that the frequency of a wave of given
wavelength and amplitude should be the same both for waves travelling in
one and the opposite directions. Alternatively, these two conditions are
consequences of the hermitian property of the coefficients of the amplitudes
of the waves in the right-hand side of the equations (3).

Since $\omega_k^2$ is a periodic function of $\theta_1$, $\theta_2$ and $\theta_3$ we can express it as a
three-dimensional Fourier-series in the form

$$\omega_k^2 = \sum_{n_1} \sum_{n_2} \sum_{n_3} \sum_{n=\infty}^{n=-\infty} A_{n_1,n_2,n_3} e^{i(n_1\theta_1 + n_2\theta_2 + n_3\theta_3)}$$

(5)

where the summation extends over all integral values of $n_1$, $n_2$ and $n_3$ from
$-\infty$ to $+\infty$.

If we use a single symbol $n$ to denote the triplet $(n_1,n_2,n_3)$ we can rewrite
(5) also in the form

$$\omega_k^2 = \sum_{n} A_n e^{i\alpha.n}$$

(6)

Since $\omega_k^2$ is real, the coefficients of $e^{i(n_1\theta_1 + n_2\theta_2 + n_3\theta_3)}$ and $e^{-i(n_1\theta_1 + n_2\theta_2 + n_3\theta_3)}$
in (5) should be complex conjugates. Hence we have

$$A_n = \bar{A}_{-n}$$

(7)

Now by writing $-\alpha$ for $\alpha$ in (6), we get

$$\omega_k^2 (-\alpha) = \sum_{n} A_n e^{-i\alpha.n}$$

(8)

Since from condition (iii), $\omega_k^2 (-\alpha) = \omega_k^2 (\alpha)$ we see by a comparison
of (6) and (8) that

$$A_n = A_{-n}$$

(9)

Combining (7) and (9) we get

$$A_n = \bar{A}_{-n} = \bar{A}_n$$

(10)
or $A_n$ is real.

We can therefore rewrite (5) as

$$\omega_k^2 = \sum_{n_1,n_2,n_3} A_{n_1,n_2,n_3} \cos (n_1\theta_1 + n_2\theta_2 + n_3\theta_3)$$

= $A_{000} + 2 \sum_{n} A_n \cos \alpha.n$

(11)

where the summation now is over all lattice points on and above any one
of the lattice planes $d_1 = 0$ or $d_2 = 0$ or $d_3 = 0$. 
We shall assume that the series obtained by differentiating term by term the sum on the right-hand side of (11) converges uniformly for all values of \( \theta_1, \theta_2 \) and \( \theta_3 \) in the interval \((0, 2\pi)\). Then, we have

\[
2\omega_k \frac{d\omega_k}{da} = -2 \sum A_n e_n \sin a_n \quad (12)
\]

Now, when \( \theta_1, \theta_2 \) and \( \theta_3 \) each takes one of the values 0 or \( \pi \), \( \sin a_n \) (i.e.) \( \sin (n_1\theta_1 + n_2\theta_2 + n_3\theta_3) \) is equal to zero. Hence if

\[
\omega_k \neq 0
\]

for these values of \( \theta_1, \theta_2 \) and \( \theta_3 \), we find from (12) that

\[
d\omega_k \quad \text{whenever} \quad \theta_1 = 0 \text{ or } \pi; \\
\quad \theta_2 = 0 \text{ or } \pi; \\
\quad \theta_3 = 0 \text{ or } \pi
\]

(14)

When \( \theta_1 = 0; \theta_2 = 0; \theta_3 = 0 \), it can be proved that three of the roots of (4) will become zero and hence the condition (13) is not satisfied. These are the limiting cases of elastic vibrations of long wavelength in the crystal and for them, since \( \omega_k \to 0 \) as \( a \to 0 \)

\[
\lim_{a \to 0} \frac{\omega_k}{a} = \frac{d\omega_k}{da} \quad (k = 1, 2, 3),
\]

and therefore the group and wave velocities become identical with the velocities of propagation of the elastic vibrations in the crystal lattice.

The eight set of cases considered above now yield a total number of \( 24p \) frequencies. Leaving out of these the three degrees of freedom pertaining to pure translations and for which, as we have seen, the group velocity is non-zero being equal to its wave velocity, we get \((24p - 3)\) frequencies for which the group velocity of the waves vanishes. The modes associated with these frequencies now possess a simple geometric description. By substituting the values of 0 or \( \pi \) for \( \theta_1, \theta_2 \) and \( \theta_3 \) in (2'), it can easily be seen that in all the \((24p - 3)\) cases referred to above, equivalent atoms in adjacent cells vibrate with the same amplitude and with the same or opposite phases along one, two or all three of the Bravais axes of the crystal. Since the group velocity is zero, any disturbance with these frequencies remains centred in the region of its origin. Further, the phase relationships for these \((24p - 3)\) modes are exactly the same as those demanded for the normal vibrations of a connected system of particles.