THE DYNAMICAL THEORY OF THE DIAMOND LATTICE. I.

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1. Introduction.

The evaluation of the so-called characteristic frequency of the diamond lattice is of considerable importance and interest when one realises its relation with the specific heat and other physical properties of diamond. The problem has consequently attracted the attention of many theorists. Einstein was the first to predict the characteristic frequency to be 909 cm.\(^{-1}\). Later, Nernst and Lindemann\(^2\) calculated the frequency to be 1833 cm.\(^{-1}\) from their specific heat measurements and their formula. A little later Debye\(^3\) calculated the maximum value of the characteristic frequency to be 1250 cm.\(^{-1}\) from his specific heat formula. A recalculation by Schroedinger\(^4\) gave 1296 cm.\(^{-1}\). The first quantitative investigation of the atomic lattice under the so-called elastic forces was undertaken by Born.\(^5\) He investigated the vibrations of the unit cell of diamond containing only eight atoms and then calculated the characteristic frequency to be 990 cm.\(^{-1}\) which is not far from that of Einstein's simple calculation. The above comprise, we think, the various theoretical calculations.

The infra-red absorption spectrum of diamond has been successively studied by Julius, Ångström and by Reinkober\(^6\) and recently with special thoroughness by Robertson, Fox and Martin.\(^7\) The investigations of Julius and Ångström indicate absorptions in regions with the frequencies 3330 cm.\(^{-1}\), 1940 cm.\(^{-1}\) and 1250 cm.\(^{-1}\), the last being very prominent. On the other hand, Reinkober found absorptions in the regions with the frequencies 3333

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cm\textsuperscript{-1}, 2439 cm\textsuperscript{-1}, 2084 cm\textsuperscript{-1} and 709 cm\textsuperscript{-1} and did not obtain the absorption with the frequency 1250 cm\textsuperscript{-1} reported by Julius and Ångström. This discrepancy has been brought into prominence by the recent work of Robertson and his collaborators.\textsuperscript{7} They advance the view that there are two types of diamond, one having absorptions in regions 3400 cm\textsuperscript{-1}, 2480 cm\textsuperscript{-1}, 2005 cm\textsuperscript{-1} and 1289 cm\textsuperscript{-1} while the other has the same absorptions except the one at 1289 cm\textsuperscript{-1}. The absorption in the region 1289 cm\textsuperscript{-1} has three maxima at $C_a$ 1372 cm\textsuperscript{-1}, $C_\beta$ 1289 cm\textsuperscript{-1} and $C_y$ 1208 cm\textsuperscript{-1}, the intensity of $C_a$ being considerably smaller than that of $C_\beta$ and $C_y$. They could not confirm the feeble band in the region with the frequency 709 cm\textsuperscript{-1} reported by Reinkober.

The Raman spectrum of diamond was first reported upon simultaneously by Ramaswamy\textsuperscript{8} and by Robertson and Fox.\textsuperscript{7} Later on Bhagavantam\textsuperscript{9} published a very striking investigation of the Raman spectra of numerous diamonds, including especially those of two very large dimensions (one of 20 carats and another of 143 carats) and recorded not only the remarkably strong line with the frequency shift 1332 cm\textsuperscript{-1} reported by the earlier investigators but also other faint lines on either side of this line, having the frequency shifts 1158 cm\textsuperscript{-1}, 1288 cm\textsuperscript{-1}, 1382 cm\textsuperscript{-1}, 1431 cm\textsuperscript{-1}, 1480 cm\textsuperscript{-1} and 1585 cm\textsuperscript{-1}. These additional lines were obtained most clearly with a brilliant white stone of 20 carats apparently belonging to the Reinkober class. It will be noticed that the faint Raman lines with the shifts 1288 cm\textsuperscript{-1} and 1382 cm\textsuperscript{-1} reported by Bhagavantam coincide with the positions of the infra-red absorption bands at 1289 cm\textsuperscript{-1} and 1372 cm\textsuperscript{-1}, barely noticeable in the Reinkober type of diamond and prominently observed in the Julius and Ångström type of diamond. Bhagavantam found that the intensity of the principal Raman line 1332 cm\textsuperscript{-1} varies not only with the size of the diamond but also with the class of the diamond; the line is in fact observed with difficulty in the case of certain diamonds which emit a blue fluorescence. Robertson and his collaborators found the principal Raman line undeviated in position with all diamonds examined by them. They suggest that the normal mode of vibration responsible for the principal Raman line is also responsible for the strong infra-red absorption with the frequency 1289 cm\textsuperscript{-1}. If this is the case, it would be difficult to understand why the latter should be present in some diamonds and absent in some others. If the normal mode of the lattice responsible for the principal Raman line is optically active, we should expect it to manifest itself in the infra-red absorption of all diamonds. Further, the difference between 1332 cm\textsuperscript{-1} and 1289 cm\textsuperscript{-1} appears too great to be


ignored. These objections would not arise if we regard that the faint
Raman line with the shift 1288 cm.\(^{-1}\) and the infra-red absorption at 1289
\(\text{cm.}^{-1}\) in the Julius and Ångström type of diamond as due to the same origin.
Why this line should behave differently in the two types of diamond would,
however, remain to be explained.

According to Bhagavantam, the scattered radiation with the principal
Raman frequency shift is not well polarised contrary to the earlier report of
Ramaswamy.

The presence of three fluorescent bands\(^6\) at 4131 A.U., 4157 A.U., and
4174 A.U. and of a continuous spectrum with its head at about 4240 A.U.
in the Raman spectrum of diamond is also a fact of great interest.

The purpose of this investigation is to formulate the equations of
vibratory motion of the whole lattice, to obtain the expressions for the
frequencies of certain typical normal modes of vibration of the
lattice and to interpret the observed vibration spectra. As a result
of this investigation, we are led to a very simple and striking interpretation
of the origin of the principal frequency shift observed in the Raman
effect of diamond. Following Bragg\(^10\) and others we can regard the
diamond lattice as the super-position of two cubic face-centred lattices
interpenetrating one another in a manner such that each atom of one
lattice is at the centre of gravity of four equally nearest atoms of the
other lattice. The origin of the principal Raman frequency is due to the
vibration of the two lattices relative to one another, each being considered as
rigid. The vibration can take place in any direction in space, for it is triply
degenerate. The same type of vibration would not be active (first order) in
the Raman effect of the rock salt lattice as has been shown by Fermi and
Rasetti,\(^11\) though the sodium atoms form one cubic face-centred lattice and
the chlorine atoms form another face-centred cubic lattice, for the interpen-
etration of the two component lattices is such that they form again a face-
centred cubic lattice in which the elements of the polarisability tensor vanish
to the first order for the vibration of the lattices relative to one another.
The vibration of the two component lattices of diamond relative to one
another is not infra-red active since all the atoms are homonuclear.

2. The internal force-system of the lattice.

In my investigation\(^12\) of the normal modes of vibration of the \(AB_4\)
molecule having tetrahedral symmetry, it was pointed out that the

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\(^{10}\) W. H. Bragg and W. L. Bragg, *X-rays and Crystal Structure.*


three forces' system comprised by the primary valence forces, the directed valence forces and the repulsive forces is a fair approximation to the correct one and that the correct one was fairly accounted for by choosing the suitable type of intra-valence forces whose contribution towards the potential energy of the molecule is constituted by the cross terms of the variations of the opposite tetrahedral angles. (The idea of intra-valence forces was first put forward by Cross and Van Vleck.13 Their idea has been very helpful to interpret the observed spectra of some types of polyatomic molecules.) Now, we may assume the same type of the internal force-system for the whole diamond lattice. This force-system does not differ greatly from the one assumed by Born4 if we neglect the repulsive forces and the intra-valence forces in our force-system. The value of our primary valence constant is different from that of his, for he defines it to be the force which would double the bond following the point of view of elasticity, while we define it as the force which would effect a unit displacement. With regard to our notation of the directed valence constant, we slightly differ from the current terminology. For example if ‘θ’ is the variation of the valence angle bound by two symmetrical bonds, the contribution towards the potential energy function is written as \( \frac{1}{2} k l^2 \theta^2 \) where ‘l’ is the length of the bonds. But the same terminology cannot be applied to denote the contribution towards the potential energy function due to the variation ‘θ’ of the valence angle bound by two unsymmetrical bonds whose lengths are different, for we can give no preference to either of the bonds. If we write the said contribution as \( \frac{1}{2} K \theta^2 \), the notation would be applicable in all cases. (\( k = \frac{K}{l^2} \) in the first case.) Recently Bonnet14 has used the same notation as that of ours.

3. The structure of the diamond lattice.

According to Bragg10 we can regard the diamond lattice to be made up of two cubic face-centred lattices, one interpenetrating the other in a manner such that each atom of one lattice is at the centre of gravity of four equally nearest atoms of the other lattice. Any atom is bound to its adjacent four atoms of the other lattice by chemical bonds at tetrahedral angles. Fig. 1 shows the structure of the lattice. All the whites belong to one cubic face-centred lattice and all the blacks belong to the other lattice. The coordinates of the atoms of

the white lattice may be defined by three integral parameters \( l(a, b, c) \) by the relations

\[
a = \frac{2p}{\sqrt{3}} (b + c), \quad \beta = \frac{2p}{\sqrt{3}} (c + a), \quad \gamma = \frac{2p}{\sqrt{3}} (a + b)
\]

where \( a, \beta \) and \( \gamma \) are the cartesian coordinates of the white atom referred to by the parameters \( a, b \) and \( c \). Similarly the coordinates of the atoms of the black lattice may be defined by three integral parameters \( l'(a', b', c') \) by the relations

\[
a' = \frac{p}{\sqrt{3}} (1 + 2b' + 2c'), \quad \beta' = \frac{p}{\sqrt{3}} (1 + 2c' + 2a'), \quad \gamma' = \frac{p}{\sqrt{3}} (1 + 2a' + 2b')
\]

where \( a', \beta' \) and \( \gamma' \) are the cartesian coordinates of the black atom referred to by the parameters \( a', b' \) and \( c' \). The four directions characteristic of the lattice are denoted by \( K, L, M \) and \( N \). Now any white atom is connected to four black atoms along the directions \( K, L, M \) and \( N \) and we denote the said connections by the suffixes \( l' r \), where \( r = K, L, M, N \). To specify the lengths in the four directions we introduce the letters \( t, f, m \) and \( n \). For example \( r_{l' r} \) denotes the length of the bond between the atom \( l \) and the nearest black atom \( l' \) in the direction \( r \), \( (r = K, L, M, N \).

The same terminology applies to the black atoms. \( r_{l' l} \) denotes the length of the bond between the black atom \( l' \) and the nearest white atom \( l \) in the direction \( r \), \( (r = K, L, M, N \).

We denote those at \( l \) by

\[
a_l^{(r)} \text{ where } (rs) = KL, KM, KN, LM, MN, NL.
\]

\*
\* \( p \) is the distance between any two connected atoms.

\† The letters in the suffixes are slightly smaller than those referred to in the lines.
Similarly, the angles at $l'$ are denoted. For example $a_{l'(rs)}^{(l)}$ denotes the tetrahedral angle at $l$ bound by directions parallel to $r$ and $s$. Then we consider another type of variations. Any atom of any one lattice has twelve equally nearest atoms of its own species. It can be seen that there are four plane hexagons having corners at some six of the twelve atoms. We denote the twelve distances by

$$t_{l'(rs)}^{il}$$ and $$t_{l'(rs)}^{il'},$$ where \( (rs) = KL, KM, KN, LM, MN, NL \) \( (tu) = LK, MK, NK, ML, NM, LN \).

For example $t_{l'(rs)}^{il}$ denotes the distance between the white atom $l$ and the nearest white atom $l_{(rs)}$ whose nearest black atom in the direction $s$ is nearest to $l$ in the direction $r$. The zero suffixes in the above lengths and angles have been introduced to denote their values in the equilibrium configuration. Their variations from the equilibrium configuration are denoted by dropping the zero suffixes and not by introducing $\delta$ or $\Delta$ as usual. The above procedure is adopted for convenience. Now it is quite easy to see by simple geometry

$$p \cdot a_{l'(rs)}^{(l)} = \sqrt{3}, t_{l'(rs)}^{il'} = \sqrt{2}. (r_{l'r'} + g_{l'i})$$

where $l'$ and $l_{rs}$ are nearest atoms to $l$ in the directions $r$ and $s$ respectively and $p$ is the distance between any two connected atoms. If so, it is quite easy to see that $t_{l'(rs)}^{il'} = t_{l'(rs)}^{il'}$. Such similar relations hold good also at all $l'$.

The relations are correct to the first order. It can also be seen that

$$\sum a_{l'(rs)}^{(l)} = \sum a_{l'(rs)}^{il'} = 0$$

by the help of the relations (1) and (3), the latter to be given later. That is, the sum of the six variations of the valence angles at any atom of the lattice is zero to the first order.

4. The equations of vibratory motion of the lattice in the cartesian system.

A crystal lattice containing $(N)$ atoms has $(3N)$ degrees of freedom in space. We can choose the $(3N)$ variations of the cartesian coordinates of the atoms of the lattice as its coordinates to specify its disturbed configuration from its initial one. Three of the coordinates correspond to the uniform translation of the whole lattice along the axes of reference. The remaining $[3(N-1)]$ coordinates correspond to the internal coordinates of the lattice. They may be chosen by the $(3N)$ cartesian variations themselves but subjecting them to the three relations

$$\sum x_{l} + \sum x_{l'} = 0
\sum y_{l} + \sum y_{l'} = 0
\sum z_{l} + \sum z_{l'} = 0$$

(2)
which preserve the constancy of the linear momentum of the lattice, where
\(x_l, y_l, z_l\) are the variations of the cartesian coordinates of the atom \(l\) and
\(x_{l'}, y_{l'}, z_{l'}\) are the variations of the cartesian coordinates of the atom \(l'\).

Now the cartesian variations are related to \(\mathbf{k}'\)'s, \(\mathbf{l}'\)'s, \(\mathbf{m}'\)'s and \(\mathbf{n}'\)'s by the relations
\[
\mathbf{r}_{ll'} = (x_l - x_{l'}) + (y_l - y_{l'}) + (z_l - z_{l'})
\]
where \(\mathbf{r} = \mathbf{k} | \mathbf{l} | \mathbf{m} | \mathbf{n} \)
\[
\mathbf{t}_{ll'}^{(rs)} = (x_l - x_{l(r)}) + (y_l - y_{l(r)}) + (z_l - z_{l(r)})
\]
\[
\mathbf{t}_{ll'}^{(tn)} = (x_l - x_{l(t)}) + (y_l - y_{l(t)}) + (z_l - z_{l(t)})
\]
where \(\mathbf{t}_{ll'}^{(rs)} = \mathbf{k}l | \mathbf{m}l | \mathbf{n}l | \mathbf{k}r | \mathbf{m}r | \mathbf{n}r \)
and other relations at \(l'\) where \(\mathbf{k}_{ll'}^{(rs)}, \mathbf{n}_{ll'}^{(rs)}\) and \(\mathbf{l}_{ll'}^{(rs)}\) are the direction cosines of the line joining the white atom \(l\) and the black atom \(l'\) and \(\mathbf{r}_{ll'}^{(rs)}\) and others denote the direction cosines of the line joining the atoms \(l\) and \(l'(rs)\) in the equilibrium configuration. The relations are correct to the first order.

The kinetic energy \(T\) of the lattice is given by the form
\[
2T = M \sum_l (\dot{x}_l^2 + \dot{y}_l^2 + \dot{z}_l^2) + M \sum_{l'} (\dot{x}_{l'}^2 + \dot{y}_{l'}^2 + \dot{z}_{l'}^2)
\]
where \(M\) is the mass of the carbon atom. The potential energy \(V\) of the lattice under the three forces' system and the intra-valence force-system spoken of in section (2) is given by the form
\[
2V = K \sum_l \sum_{l'} (\dot{x}_l^{(rs)} + \dot{y}_l^{(rs)} + \dot{z}_l^{(rs)})
+ K' \sum_l \sum_{l'} (\dot{x}_{l'}^{(rs)} + \dot{y}_{l'}^{(rs)} + \dot{z}_{l'}^{(rs)})
+ 2K'' \sum_l \sum_{l'} (\dot{x}_l^{(rs)} + \dot{y}_l^{(rs)} + \dot{z}_l^{(rs)})
\]
where \(K\) is the force constant of the primary valence bonds, \(K'\) is the force constant of the directed valence of the bonds at \(l\) and \(l'\), \(K''\) is the force constant of the repulsions between nearest white or black atoms and \(K'''\) is the intra-valence force constant at the atoms \(l\) and \(l'\). The various variations in the potential energy function are connected to the cartesian variations by the relations (3) and (1).

We will now obtain the equations of vibratory motion of the lattice in the cartesian system by following the usual Lagrange method. Various

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* The symbol \(\mathbf{t}_{ll}^{(rs)}\) occurs in the equations.
differentiations of the potential energy function with respect to the cartesian coordinates are carried out by the help of the relations (3) and (1). We will only give a typical cartesian equation.

\[- M \ddot{r}_i = K \sum r_{r_i} \xi_{r_i} + \frac{K'}{p} \sum a^{rs}_i \left( \xi_{r_i} + \xi_{r_i} \right) \]

\[+ \frac{K'}{p} \sum a^{rs}_i \left( \sqrt{3} \xi_{r_i} - \sqrt{2} \xi_{r_i} \right) + \sum a^{rs}_i \left( \sqrt{3} \xi_{r_i} - \sqrt{2} \xi_{r_i} \right) \]

where \( \mu_x, \mu_y \) and \( \mu_z \) are Lagrange's undetermined multipliers corresponding to the relations (2).

If \( (N) \) is the number of atoms in the lattice the number of equations is of the order \( (3N) \) with the three constraints. The frequencies of the normal modes of vibration of the lattice are obtained by solving the secular determinantal equation corresponding to the above \( (3N) \) equations. The order of the determinant may be regarded as infinite by letting \( (N) \rightarrow \infty \). But the actual solution of the secular equation obtained by the cartesian equation presents innumerable difficulties. But at times we can recognise certain factors of the secular equation by seeking certain independent linear transformations, for the roots of the secular equation are invariant with respect to all independent linear transformations. Supposing it is possible to transform the \( (3N) \) independent equations to \( (3N + P) \) equations by certain schemes of linear transformations, then \( (P) \) equations of the transformed ones will be dependent. If it is possible to select \( (3N) \) independent equations of the transformed ones and solve the secular equation corresponding to them, or if it is possible to select a few independent equations and solve the secular equation corresponding to them, the factors will be the same as those of the original secular equation.

5. Transformation of the cartesian equations and a typical root of the secular equation.

Following the ideas of section 4, we transform the \( (3N) \) cartesian equations to \( (8N) \) equations by the schemes of transformations comprised by the relations (3) and (1). That is, we find the equations of motion of all the variations of the internuclear distances between connected atoms which are \( (2N) \) in number and all the variations of the valence angles at all atoms.
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which are \((6N)\) in number. We will only give two typical equations.* The suffix \(l_r\) refers to the white atom nearest to \(l_r\) in the direction \(i\); \(r, s, t = K, L, M, N\).

\[
M \frac{d}{dt} \mathbf{v}_r = 2(K + 2K') \left( \mathbf{v}_r + \mathbf{m}_v + \mathbf{n}_v + \mathbf{I}_v + \mathbf{m}_v^{KN} + \mathbf{n}_v^{KN} \right) - \frac{2K''}{3} \left( \mathbf{v}_r + \mathbf{m}_r + \mathbf{n}_r + \mathbf{I}_r + \mathbf{m}_r^{KN} + \mathbf{n}_r^{KN} \right)
\]

\[
- \frac{\sqrt{2}}{3p} \left\{ \left( K' - K'' \right) - K'' p^2 \right\} \left( \mathbf{a}_l + \mathbf{a}_M + \mathbf{a}_N + \mathbf{a}_L + \mathbf{a}_K + \mathbf{a}_L' + \mathbf{a}_K' \right)
\]

\[
+ \frac{K''}{3p} \left( \mathbf{a}_l^{KL} + \mathbf{a}_m^{KL} + \mathbf{a}_n^{KL} + \mathbf{a}_L^{KL} + \mathbf{a}_M^{KL} + \mathbf{a}_N^{KL} + \mathbf{a}_K^{KL} + \mathbf{a}_L'^{KL} + \mathbf{a}_K'^{KL} \right)
\]

\[
- \frac{\sqrt{2}}{3p} \left( 2K' + K'' p^2 \right) \left( \mathbf{a}_l^{KL} + \mathbf{a}_m^{KL} + \mathbf{a}_n^{KL} + \mathbf{a}_L^{KL} + \mathbf{a}_M^{KL} + \mathbf{a}_N^{KL} + \mathbf{a}_K^{KL} + \mathbf{a}_L'^{KL} + \mathbf{a}_K'^{KL} \right)
\]

\[
- \frac{2K''}{3p} \left( \mathbf{a}_l^{LM} + \mathbf{a}_m^{LM} + \mathbf{a}_n^{LM} + \mathbf{a}_L^{LM} + \mathbf{a}_M^{LM} + \mathbf{a}_N^{LM} + \mathbf{a}_K^{LM} + \mathbf{a}_L'^{LM} + \mathbf{a}_K'^{LM} \right)
\]

\[
- \frac{\sqrt{2}}{3p} \left( \mathbf{a}_l^{MN} + \mathbf{a}_m^{MN} + \mathbf{a}_n^{MN} + \mathbf{a}_L^{MN} + \mathbf{a}_M^{MN} + \mathbf{a}_N^{MN} + \mathbf{a}_K^{MN} + \mathbf{a}_L'^{MN} + \mathbf{a}_K'^{MN} \right)
\]

\[
- \mathbf{M} \mathbf{a}_l^L = \frac{M\sqrt{2}}{p} \left( \mathbf{v}_r + \mathbf{m}_v + \mathbf{n}_v + \mathbf{I}_v + \mathbf{m}_v^{KN} + \mathbf{n}_v^{KN} \right) - \frac{\sqrt{2}}{p} \left( K + 3K' \right) \left( \mathbf{v}_r + \mathbf{m}_r + \mathbf{n}_r + \mathbf{I}_r + \mathbf{m}_r^{KN} + \mathbf{n}_r^{KN} \right)
\]

\[
- \frac{\sqrt{2}}{p} \left( K + 2K' \right) \left( \mathbf{v}_r + \mathbf{m}_r + \mathbf{n}_r + \mathbf{I}_r + \mathbf{m}_r^{KN} + \mathbf{n}_r^{KN} \right) + \frac{K''}{p} \left( \mathbf{a}_l^{KL} + \mathbf{a}_m^{KL} + \mathbf{a}_n^{KL} + \mathbf{a}_L^{KL} + \mathbf{a}_M^{KL} + \mathbf{a}_N^{KL} + \mathbf{a}_K^{KL} + \mathbf{a}_L'^{KL} + \mathbf{a}_K'^{KL} \right)
\]

\[
- \frac{\sqrt{2}}{p} \left( 2K' + K'' p^2 \right) \left( \mathbf{a}_l^{KL} + \mathbf{a}_m^{KL} + \mathbf{a}_n^{KL} + \mathbf{a}_L^{KL} + \mathbf{a}_M^{KL} + \mathbf{a}_N^{KL} + \mathbf{a}_K^{KL} + \mathbf{a}_L'^{KL} + \mathbf{a}_K'^{KL} \right)
\]

\[
- \frac{2K''}{p} \left( \mathbf{a}_l^{LM} + \mathbf{a}_m^{LM} + \mathbf{a}_n^{LM} + \mathbf{a}_L^{LM} + \mathbf{a}_M^{LM} + \mathbf{a}_N^{LM} + \mathbf{a}_K^{LM} + \mathbf{a}_L'^{LM} + \mathbf{a}_K'^{LM} \right)
\]

\[
- \frac{\sqrt{2}}{p} \left( \mathbf{a}_l^{MN} + \mathbf{a}_m^{MN} + \mathbf{a}_n^{MN} + \mathbf{a}_L^{MN} + \mathbf{a}_M^{MN} + \mathbf{a}_N^{MN} + \mathbf{a}_K^{MN} + \mathbf{a}_L'^{MN} + \mathbf{a}_K'^{MN} \right)
\]

\[
+ \frac{1}{2} \left( \frac{3K'}{p^2} + \frac{K''}{p^2} + 3K'' \right) \mathbf{a}_l^L + \frac{1}{2} \left( \frac{K'}{p^2} + \frac{3K''}{p^2} \right) \mathbf{a}_l^{MN}
\]

\[
+ \frac{1}{2} \left( \frac{3K'}{p^2} + K'' \right) \left( \mathbf{a}_l^{LM} + \mathbf{a}_m^{LM} + \mathbf{a}_n^{LM} + \mathbf{a}_L^{LM} + \mathbf{a}_M^{LM} + \mathbf{a}_N^{LM} + \mathbf{a}_K^{LM} + \mathbf{a}_L'^{LM} + \mathbf{a}_K'^{LM} \right)
\]

\[
+ \frac{3K'}{p^2} \left( \mathbf{a}_l^{KN} + \mathbf{a}_m^{KN} + \mathbf{a}_n^{KN} + \mathbf{a}_L^{KN} + \mathbf{a}_M^{KN} + \mathbf{a}_N^{KN} + \mathbf{a}_K^{KN} + \mathbf{a}_L'^{KN} + \mathbf{a}_K'^{KN} \right)
\]

\[
\left( \frac{K'}{p^2} + K'' \right) \left( \mathbf{a}_l^{KL} + \mathbf{a}_m^{KL} + \mathbf{a}_n^{KL} + \mathbf{a}_L^{KL} + \mathbf{a}_M^{KL} + \mathbf{a}_N^{KL} + \mathbf{a}_K^{KL} + \mathbf{a}_L'^{KL} + \mathbf{a}_K'^{KL} \right)
\]

\[
+ \frac{1}{2} \left( \frac{K'}{p^2} - K'' \right) \left( \mathbf{a}_l^{KN} + \mathbf{a}_m^{KN} + \mathbf{a}_n^{KN} + \mathbf{a}_L^{KN} + \mathbf{a}_M^{KN} + \mathbf{a}_N^{KN} + \mathbf{a}_K^{KN} + \mathbf{a}_L'^{KN} + \mathbf{a}_K'^{KN} \right)
\]

The number of equations is of the order \((8N)\) and we will have to select only \((3N)\) independent equations out of them. At present we do not concern

* One has to remember the usual cosine formula in transforming the cartesian equations.
ourselves with the reduction and factorisation of the secular equation but will find a typical factor of the equation. To recognise it we introduce the following linear transformations:--

\[ \Phi_\tau = \sum_l r_{l\nu} \]

It can be easily seen that \( \sum \Phi_\tau = 0 \). Also one can find that

\[ \sum_i \left( a_i^{\nu_l} + a_i^{\nu_m} + a_i^{\mu_k} - a_i^{\mu_n} - a_i^{\nu_k} - a_i^{\nu_n} \right) = \sum_{\nu} \left( a_{\nu_l}^{\mu_k} + a_{\nu_m}^{\mu_k} + a_{\nu_l}^{\mu_n} - a_{\nu_m}^{\mu_n} - a_{\nu_l}^{\nu_k} - a_{\nu_m}^{\nu_k} \right) \]

\[ = -\frac{\sqrt{2}}{p} \left( 3 \phi_\mu - \phi_\lambda - \phi_\sigma - \phi_\nu \right) \]

\[ = -\frac{4 \phi_\kappa \sqrt{2}}{p} \]

The equations of motion corresponding to \( \Phi \)'s are

\[ -\ddot{\Phi}_\tau = \frac{8}{3M} \left( K + \frac{8(K'-K'')}{p^2} \right) \Phi_\tau \]

\( \tau = \kappa, \lambda, \mu, \nu \).

We can regard any three of the \( \Phi \)'s as independent and the fourth as the sum of the other three with the negative sign. So the mode of vibration corresponding to \( \Phi \)'s is triply degenerate. The frequency of the modes is given by

\[ \nu = \frac{1}{2\pi c} \sqrt{ \left[ \frac{8}{3M} \left( K + \frac{8(K'-K'')}{p^2} \right) \right] } \]

The atoms 3, 12, 13 and 14 are not shown in the figure.
The normal mode $\Phi_\kappa$ is described when all

$$\mathbf{h}_{\mathbf{u}_\kappa} = 2x, \quad \mathbf{l}_{\mathbf{v}_\kappa} = \mathbf{m}_{\mathbf{u}_\kappa} = \mathbf{n}_{\mathbf{u}_\kappa} = -\frac{2x}{3},$$

$$a_r^{\alpha} = a_r^{\alpha'} = a_r^{\kappa} = -a_r^{\alpha'} = -a_r^{\kappa} = -\frac{4x\sqrt{2}}{3p}$$

where $x$ is the distance moved by the white atoms and the distance moved by black atoms in the opposite direction. The normal vibration $\Phi_\kappa$ corresponds to the vibration of the two component lattices relative to one another considered as rigid in the direction $\kappa$.

**6. A simple derivation of the lattice oscillation frequency.**

We will also give a simple derivation of the expression for the frequency of the modes $\Phi$'s. Let us confine our attention to the mode $\Phi_\kappa$. We will make use of the simple principle that in any particular normal mode of vibration of a system any component of the system will have also the same frequency as that of the normal mode, for there is only one periodic coordinate. Let us consider the components of all forces which are responsible for the motion of $\mathbf{4}'$ along $(\mathbf{4}' 4)$. If we find all those terms in the potential energy function which involve the cartesian coordinates of $\mathbf{4}'$, the total force acting against the motion of $\mathbf{4}'$ can be easily calculated. In the mode under consideration all the white atoms move in the same direction by a distance $x$ and all the black atoms move in the opposite direction by a distance $x$. The components of the primary valence forces which influence the motion of $\mathbf{4}'$ are those due to the variations of the bonds $\mathbf{4}' 4'$, $\mathbf{1} 4'$, $\mathbf{2} 4'$ and $\mathbf{3} 4'$. The force arising from the variation of $\mathbf{4}' 4'$ is $2Kx$ which acts against the direction of motion of $\mathbf{4}'$. One can easily show that the bonds $\mathbf{1} 4'$, $\mathbf{2} 4'$ and $\mathbf{3} 4'$ suffer each the change $-\frac{2x}{3}$. The component of the forces along the three bonds acting against the direction of motion of $\mathbf{4}'$ is $\frac{2Kx}{3}$. It can be easily seen that repulsive forces between adjacent like atoms are not at all operative in this mode. The component of the directed valence forces which influence the motion of $\mathbf{4}'$ are those arising due to the variations of the six valence angles at $\mathbf{4}'$, the three valence angles at $\mathbf{1}'$ containing the $\mathbf{1} 4'$ bond, the three valence angles at $\mathbf{2}'$ containing the $\mathbf{2} 4'$ bond and the three valence angles at $\mathbf{3}'$ containing the $\mathbf{3} 4'$ bond. It can be easily seen that the component of forces arising from the variations of the angles at $\mathbf{4}'$ on the atom $\mathbf{4}'$ is zero along $(\mathbf{4}' 4')$ in this normal mode. Let us first consider $\theta_{14}'$ the variation of the valence angle bound by $(\mathbf{4}' 4)$ and $(\mathbf{1} 4)$. It can be shown that

$$p \theta_{14}' = \sqrt{3} d_{14}' - \sqrt{2}(d_{14} + d_{44}') = -\sqrt{2}(d_{14} + d_{44}')$$
where $d_{rs}$ denotes the variation of the internuclear distance between the atoms $r$ and $s$. $d_{14'}$ is zero in the normal mode under consideration. The force arising from the variation $\theta_{14'}$ acting against the direction of motion of $4'$ is

$$K' \theta_{14'} \times \frac{\partial^2 \theta_{14'}}{\partial x_{14}} = \frac{K'}{\rho^2} \left[ -\sqrt{2} (d_{14} + d_{14'}) \right] \left[ -\sqrt{2} \left( -\frac{1}{2} + 1 \right) \right] = \frac{16 K'x}{9 \rho^2}$$

Therefore the total force acting along $(4'4')$ due to $\theta_{14'}$, $\theta_{24'}$ and $\theta_{34'}$ is $\frac{16 K'x}{3 \rho^2}$. Similarly it can be shown that the other three angles at $4'$ contribute $\frac{16 K'x}{3 \rho^2}$. Following the same procedure we can show that the component of the valence forces along $(44')$ due to the variations $\theta_{46}$, $\theta_{47}$, $\theta_{49}$, $\theta_{410}$, $\theta_{412}$ and $\theta_{413}$ is $\frac{16 K'x}{3 \rho^2}$ and those due to $\theta_{48}$, $\theta_{411}$ and $\theta_{414}$ is $\frac{16 K'x}{3 \rho^2}$. Similarly, the contribution from the intra-valence force system may be calculated.

Then it can be seen that the total force $F$ acting on $4'$ against the direction of its motion is

$$F = -M\ddot{x} = \frac{8x}{3} \left[ K + \frac{8 (K' - K''')}{\rho^2} \right].$$

The expression for the frequency is

$$\nu = \frac{1}{2 \pi \rho} \sqrt{\frac{8}{3M} \left[ K + \frac{8 (K' - K''')}{\rho^2} \right]}.$$ 

Now, we can theoretically evaluate the value of $\nu$ in the case of diamond if we know the values of the force constants correctly. It appears that the calculations of the said constants till now made by the vibration spectra data of organic compounds are based on assumptions which are questionable. We shall not be far amiss if we take the constants to be as $K \approx 4 \times 10^6$ dyn./cm. and $(K' - K''')/\rho^2 \approx 0.2 \times 10^6$ dyn./cm. We get $\nu$ to be $1346$ cm.$^{-1}$. The agreement between $1346$ cm.$^{-1}$ and the observed $1332$ cm.$^{-1}$ corresponding to the principal Raman frequency shift is however not to be stressed, as it depends on the tentatively assumed values of the force constants.

Further work is under progress and will be reported later on. The author is highly thankful to his professor Sir C. V. Raman for his great interest and suggestions throughout the work.

7. Summary.

(1) The theoretical calculations of the characteristic frequency of diamond and the experimental results of the vibration spectra of diamond are reviewed in brief; (Section 1).

(2) The vibratory equations of motion of the diamond lattice under the three forces' system and the suitable type of intra-valence forces are
formulated. A typical factor of the secular equation is then obtained and it is found that it corresponds to the vibration of the two component cubic face-centred lattices composing the diamond lattice relative to one another, each being considered as rigid. The said vibration is triply degenerate. It appears that this vibration is Raman-active but optically inactive since all the atoms are homonuclear. Hence an explanation for the origin of the principal Raman line with the shift 1332 cm.$^{-1}$ and the absence of the infra-red band corresponding to 1332 cm.$^{-1}$ follows.