Theory of the Normal Modes of Vibration in Crystal

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The normal modes of vibration in crystal have been determined by the group-theoretical method, familiar in the theory of molecules. Secular equation for determining the frequencies of normal modes has been reduced to lower degrees by making use of the translational, crystal and \( K \)-groups. The frequency-distribution curves have been obtained for a few types of crystals, with a brief reference to 2nd order Raman-effect.

§ 1. Introduction

In order to classify the normal modes of vibration of molecules, group-theoretical method is very powerful. Each mode corresponds to a definite irreducible representation of the point group to which the molecule belongs. The secular equation for determining frequencies is reduced to the equations of lower degrees, each corresponding to a definite irreducible representation. In the present paper we have extended this general treatment to determine the normal modes in crystal.

First we develop the general theory for the case of a simple cubic lattice introducing translational normal coordinates, and then we reduce the translational dynamical matrix by the use of the irreducible representations of \( K \)-groups in special directions in reciprocal lattice space, introduced by Bouchaert-Smoluchowsky-Wigner.\(^1\) Next we apply these theories to actual crystals, especially to NaCl and diamond, and calculate the distribution functions of frequencies by the method of Houston\(^2\) assuming appropriate potential energies between atoms in the crystals. In the same way, after Born and Bradburn\(^3\) we analyse the profile of the 2nd order Raman-effect for the diamond crystal by calculating the distribution functions of over-tones and combination-tones.

§ 2. General theory for simple cubic lattice

The position of atoms in a simple cubic lattice is expressed by their integral coordinates \((l, m, n)\) in a suitable rectangular coordinate system. Consider a configuration that an atom at \((l, m, n)\) is displaced by unit amount in \(x\)-direction, the other atoms remaining in the original regular positions. We shall denote this configuration by \(e(l, m, n : x)\), and similary for the displacements in \(y\) and \(z\)-directions. Then the assembly

\[
e(l, m, n : \xi), \xi = x, y, z, -\infty < (l, m, n) < \infty
\]
constitutes the bases of infinite-dimensional vector space describing the possible displace-
ments of the atoms in the crystal. Now combine these vectors into
\[ e(k_x, k_y, k_z; \xi) = e(l, m, n; \xi) = e(l + \rho p, m + q y, n + r z) \]

which make up a normalized orthogonal system.

For the translation \( p, q, r \) in \( x, y, z \)-directions, the vector \( e(l, m, n; \xi) \) is transformed into
\[ T(p, q, r) e(l, m, n; \xi) = e(l + p, m + q, n + r; \xi) \]

and consequently
\[ T(p, q, r) e(k_x, k_y, k_z; \xi) = \exp\left\{ -i (p k_x + q k_y + r k_z) \right\} e(k_x, k_y, k_z; \xi). \]

This shows that these three vectors \( e(k_x, k_y, k_z; \xi), \xi = x, y, z \), defined for one set of \( K(k_x, k_y, k_z) \) value, are the bases of the same one-dimensional irreducible representation of the translational group. The normal coordinates of vibrations in a crystal are the linear combinations of the vectors \( e(l, m, n; \xi) \). Thus the secular equation (of an infinite order) for determining frequencies, constructed with \( e(l, m, n; \xi) \) as basis, is known to be reducible to those with dimensions not more than three, for each set of \( K \) value. The reduction is independent of the form of potential energy functions. The form of the transformation matrix \( M \) is to be the following as seen from (2.2).

\[
\begin{pmatrix}
\vdots & \vdots & \vdots \\
0 & D^{k_x k_y k_z}_{l m n} & 0 \\
\end{pmatrix}
\]

For simplicity we have given here only 9 elements of \( e(l, m, n; \xi) \). With this matrix \( M \), we shall next transform the infinite matrix \( A \) of the quantity \( V = (A v, v) \). Here \( V \) is the potential energy which is assumed to be quadratic form of the vector
\[ v = \sum_{l, m, n} e(l, m, n; \xi) u(l, m, n) + e(l, m, n; y) v(l, m, n) + e(l, m, n; z) w(l, m, n). \]

We assume that \( V \) involves only central force depending upon the distances between atoms, and further interaction between the nearest neighbours and the second nearest
neighbours are taken into consideration for the sake of simplicity. If $u$ and $\beta$ are force constants for the respective interaction, $V$ is expressed as

$$V = \frac{u}{2} \sum_{\text{1st nearest}} (u_i - u_k)^2 + \sum_{\text{2nd nearest}} \beta (u_j - u_i)^2,$$  \hspace{1cm} (2.7)

where $u_i$ is a displacement vector of $i$-th atom. We rewrite this displacement quantity by the components $u, v, \omega$ and put into (2.7). Then we obtain a quadratic form of potential energy $V$. The elements of matrix $A$ are easily known and it can easily be shown that $(l, m, n : x | l, m : x)$ element, the diagonal element of the matrix, is $u + 4\beta$, and while the non-vanishing elements off diagonal such as $(l, m, n : x | l + 1, m, n : x)$ is $-\frac{a}{2}$. Therefore $V$ consists of terms $(u + 4\beta)u(l, m, n)^2 - 2\frac{a}{2} u(l, m, n) 
\times u(l + 1, m, n) \ldots$ When $A$ is transformed by $M$, $A$ is decomposed into a number of three dimensional matrices $D(k_x, k_y, k_z)$, each labelled by one set of $K$ value. After some calculations we obtain the matrix $D(k_x, k_y, k_z)$ in the following form:

$$D(k_x, k_y, k_z) = \begin{pmatrix}
A(k_x k_y k_z) & B(k_x k_y) & B(k_x k_z) \\
B(k_y k_x) & A(k_y k_z) & B(k_y k_z) \\
B(k_z k_x) & B(k_z k_y) & A(k_z k_y)
\end{pmatrix},$$  \hspace{1cm} (2.8)

$$A(k_x k_y k_z) = (u + 4\beta) - u \cos k_x - 2\beta \cos k_y + \cos k_x \cos k_z,$$

$$B(k_x k_y) = 2\beta \sin k_x \sin k_y,$$

$$-\pi \leq k_x, k_y, k_z \leq \pi.$$  \hspace{1cm} (2.9)

(2.9) is just the same equation as one which was investigated by Born and others$^0$ from the infinite set of differential equation. But this group-theoretical method has the merits of making the form of eigenvectors (normal modes of vibration) obvious. We can obtain frequencies by solving this 3-dimensional secular equation and express the eigen-vector corresponding to each eigen-value by liner combination of vectors $e(k_x, k_y, k_z; z)$. We have to notice that these solutions can be obtained solely from the most fundamental operations of the translational group characteristic to the crystal; in this sense these eigenvectors are to be called translational normal vectors of vibrations. So far we have been concerned with the translational symmetry of the lattice. The full symmetry of the lattice is represented by a space group. So that we have to examine the representation problem concerning to the point group $O_h$, which is obtained by deviding the space group by the invariant sub-group $T$.

For one element of point group $O_h$, say, a rotation $\frac{\pi}{2}$ about $z$ axis referring to a certain fixed lattice point; $R_z(\frac{\pi}{2})$, we have

$$R_z(\frac{\pi}{2})e(l, m, n : x) = e(-m, l, n : y).$$  \hspace{1cm} (2.10)
Then following equation holds
\[
R_x(\pi/2) e(k_x, k_y, k_z : x) = \sum D^x_{lmn} R_x(\pi/2) e(l, m, n : x) = \sum D^x_{lmn} e(-m, l, n : y) = e(-k_y, k_x, k_z : y).
\]

(2.11)

We notice the transformation (2.11) is exactly the same as (2.10); that is to say, the operation of a rotation of the group \( O_h \) on the translational normal vectors \( e(K, \xi) \) can be obtained by changing the arguments \( K, \xi \) into \( K', \xi' \) in such a way that the unit vector in the direction \( \xi \) at the point \( K \) in \( K \)-space is transformed by the same operation into another unit vector in the direction \( \xi' \) at the point \( K' \). Thus we can find the representation for the elements of group \( O_h \). The dimension of representation at a general point \( k_x = k_y = k_z \) in \( K \)-space is as large as 144. Now we resolve the spurs of representation of elements of \( O_h \) which operate vectors \( e(k_x, k_y, k_z : \xi) \), and have
\[
3A_{1g,u} + 3A_{2g,u} + 6E_{g,u} + 9T_{1g,u} + 9T_{2g,u}.
\]

(2.12)

From this fact, we see that the reduction of the secular equation to less than 3 degrees will be impossible, if we do not make some simplifying assumption for potential energy. We tried to transform this 144 dimensional matrix for our specially assumed potential but in vain. Generally speaking, in the case that \( n \) atoms are included in unit cell of crystal, and they are all different from each other, they can not be combined each other by translational operations, and the secular equation for one \( K \) value would be \( 3n \) dimensions (for example 6 for NaCl), namely the transformed matrix \( \mathcal{D}(k_x, k_y, k_z) \) would be \( 3n \) dimensions. Resolution for factor group are also \( n \) times of (2.11) only. In conclusion, the secular equation can not be reduced to dimensions less than \( 3n \), by space group. But the reduction is sometimes possible at a special point or along special lines in \( K \)-space.

B.-S.-W. introduced the theory of \( K \)-group. For instance, if we collect only those elements of \( O_h \) which leaves the vector \( e(k_x, k_y, k_z : \xi) \) invariant, they constitute a sub-group of \( O_h \), which is called \((k_x, k_y, k_z : \xi)\)-group, one of \( K \)-groups. Out of these whole \( K \)-groups we pick up three \( K \)-groups only, namely \((k, k, k)\)-group, \((k, k, 0)\)-group, and \((k, 0, 0)\)-group which are interesting for us. Operating each element belonging to each \( K \)-group upon the vectors \( e(k_x, k_y, k_z : \xi) \), \( e(k_x, k_z : \xi) \), and \( e(k_x, 0, 0 : \xi) \), we obtain the following representations and resolutions by irreducible representations for individual \( K \)-group.

<table>
<thead>
<tr>
<th>(1) ((k, k, k))-group</th>
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<tbody>
<tr>
<td>Element</td>
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| Res. | \( A_1 + A_3 \)

(2.13)
(2) \((k, k, 0)\)-group

Element \(E\) \(C_2(x, y)\) \(J C_2^i(x)\) \(J C_2(x-y)\)

Class \((1)\) \((2)\) \((3)\) \((4)\)

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\]

Res. \(\Sigma_1 + \Sigma_2 + \Sigma_3\). \((2.14)\)

(3) \((k, 0, 0)\)-group

Element \(E\) \(C_2(x)\) \(C_2^s(x)\) \(J C_2^s(x)\) \(J C_2^s(y)\) \(J C_2^s(yz)\) \(J C_2^s(y-z)\)

Class \((1)\) \((2)\) \((3)\) \((4)\) \((4)\) \((5)\) \((5)\)

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Res. \(A_1 + A_3\). \((2.15)\)

Here \(C_2(x, y, z), C_2(x-y), C_4(x)\ldots\) are elements of group \(O_h\), and they show a rotation \(2\pi/3\) about the diagonal axis of \(x, y, z\) axes, a rotation \(\pi\) about the axis which bisect \(x, y, z\) axes and a rotation \(\pi/2\) about \(z\) axis \ldots\) \(J\) is an inversion with respect to the origin of the coordinates. The notation \(A_1, A_3, \Sigma_1, \Sigma_3, \Sigma_4, A_1, D_3\) represent the irreducible representations of \(K\)-groups named by \(B. - S. - W.\), out of which \(A_1, A_3\) are ones of 2-dimensions, and others of 1-dimension.

The above relation shows no repetition of the same irreducible representation and from this ground, we understand that secular equation is to be reduced down to one dimension along the above-mentioned 3 directions in \(K\)-space. The transformation matrix for obtaining the bases which give the irreducible representations have the following forms:

\[
M(k, k, k) \quad M(k, k, 0) \quad M(k, 0, 0)
\]

\[
\frac{1}{\sqrt{3}}\begin{pmatrix}
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\end{pmatrix}
\begin{pmatrix}
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1/\sqrt{2} \\
1/\sqrt{2}
\end{pmatrix}
\begin{pmatrix}
\sqrt{3}/2 \\
\sqrt{3}/2 \\
\sqrt{3}/2
\end{pmatrix}
\quad \frac{1}{\sqrt{2}}\begin{pmatrix}
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\end{pmatrix}
\begin{pmatrix}
1 \\
1 \\
0
\end{pmatrix}
\begin{pmatrix}
0 \\
0 \\
\sqrt{2}
\end{pmatrix}
\begin{pmatrix}
0 \\
0 \\
1
\end{pmatrix}
\]

\[(2.16)\]

Matrix \(M(k, 0, 0)\) shows that \(\Sigma(k, 0, 0)\) has already been reduced to 1 dimension. If we transform matrices \(\Sigma(k, k, k)\), and \(\Sigma(k, k, 0)\) by matrices \(M(k, k, k)\) and \(M(k, k, 0)\), they are completely reduced down as the following equation shows.

\[
M^{-1}(k, k, k) \Sigma(k, k, k) M(k, k, k) \quad M^{-1}(k, k, 0) \Sigma(k, k, 0) M(k, k, 0)
\]

\[
\begin{pmatrix}
A + 2B & 0 & 0 \\
0 & A-B & 0 \\
0 & 0 & A-B
\end{pmatrix}
\begin{pmatrix}
A' + B' & 0 & 0 \\
0 & A'-B' & 0 \\
0 & 0 & C'
\end{pmatrix}
\]

\[(2.17)\]
It can be generally said that when \( n \) particles included in unit cell are different from each other, the 3\( n \)-dimensional matrix \( \mathfrak{D} \) is thoroughly reduced down by \( K \)-group along 3 directions, but in the case that there are some like atoms among \( n \) there may be some interchange among them by the operations of \( K \)-group, and their representations and resolutions are different from the simple \( n \) times of degeneracy of (2·13), (2·14) and (2·15). In this case we have to calculate each representation corresponding to each type of crystal. It allows the same treatment as the case of molecules.

We applied this method to the real crystal, for example NaCl and diamond, calculated \( \mathfrak{D} \) matrices, carried out the reduction by \( K \)-groups and obtained the distribution functions of the frequencies by the method which Houston introduced. In these example assuming on special terms in potential energy, we take the type of (2·7), which are adopted generally and the value of constant ratio \( \beta/\alpha=0.05 \) as Blackmann\(^5\) and Montroll\(^6\) did.

§ 3. Application to NaCl and diamond

(1) **NaCl** This is the case \( n=2 \) in 2. As Na atom are never interchanged with Cl atom by any operation of translation, the transformation matrix corresponding to one set of \( K \) value, must have the following form (3·1). The number \((l, m, n)\) and \((l+1, m+1, n+1)\) are coordinates of Na and Cl which lie in the same unit cell.

\[
\begin{align*}
\cdots & k_x k_y k_x x_1 k_z k_y k_x y_1 k_z k_y k_x z_1 k_x k_y k_x x_2 k_z k_y k_x y_2 k_z k_y k_x z_2 \\
& k_x k_y k_x x_1 k_z k_y k_x y_1 k_z k_y k_x z_1 k_x k_y k_x x_2 k_z k_y k_x y_2 k_z k_y k_x z_2 \\
& \cdots \\
\end{align*}
\]

\[
\begin{align*}
M = l+1, m+1, n+1 : x & \cdots \\
& \cdots D_{l+m+n}^{k_y k_x} 0 \\
& \cdots D_{l+m+n}^{k_y k_x} 0 \\
& \cdots \\
\end{align*}
\]

We express potential energy by a quadratic form, and transforming the matrix \( A \) by the matrix \( M \) of (3·1) we get \( \mathfrak{D} \) matrix.

\[
A = a + 4\beta - \alpha \cos k - 4\beta \cos^2 k, \quad A' = a + 4\beta - \alpha \cos k - 2\beta \cos k - 2\beta \cos^2 k, \\
B = 2\beta \sin^2 k, \quad B' = 2\beta \sin^2 k, \\
C' = 4\beta (1 - \cos k). 
\]
Theory of the Normal Modes of Vibration in Crystal

\[ \mathcal{D}(k_x, k_y, k_z) \]

\[
\begin{pmatrix}
A(k_x, k_y, k_z)/m & B(k_x, k_y)/m & B(k_x, k_z)/m & C(k_x) & 0 & 0 \\
B(k_y, k_x)/m & A(k_y, k_x, k_z)/m & B(k_y, k_z)/m & C(k_y) & 0 & 0 \\
B(k_z, k_x)/m & B(k_z, k_y)/m & A(k_z, k_x, k_y)/m & C(k_z) & 0 & 0 \\
0 & C(k_y) & 0 & B(k_y, k_x)/M & A(k_y, k_x, k_z)/M & B(k_y, k_z)/M \\
0 & 0 & C(k_z) & B(k_z, k_x)/M & B(k_z, k_y)/M & A(k_z, k_x, k_y)/M
\end{pmatrix}
\]

(3.2)

In this equation, \( m \) and \( M \) are masses of atoms and constants \( A, B \) and \( C \) are defined as follows:

\[ A(k_x, k_y, k_z) = u + 4\beta - 2\beta \cos k_x (\cos k_y + \cos k_z), \]

\[ B(k_x, k_y) = 2\beta \sin k_x \sin k_y, \]

\[ C(k_x) = -u \cos k_x / \sqrt{mM}. \]

The transformation matrices by \( K \)-groups are the simple enlargement of (2.13) (2.14) (2.15), as shown in the following equation:

\[
\mathcal{M}(k, k, k)
\]

\[
\begin{pmatrix}
1 & 1/\sqrt{2} & \sqrt{3}/2 & -1 & 0 & 0 \\
1 & -\sqrt{2} & 0 & 1 & 0 & 0 \\
1 & 1/\sqrt{2} & -\sqrt{3}/2 & 1 & 0 & 0 \\
\frac{1}{\sqrt{3}} & 0 & 0 & 1 & 1/\sqrt{2} & \sqrt{3}/2 \\
0 & 0 & 0 & 1 & -\sqrt{2} & 0 \\
0 & 0 & 0 & 1 & 1/\sqrt{2} & -\sqrt{3}/2
\end{pmatrix}
\]

(3.3)

When \( \mathcal{D} \) matrix (3.2) are transformed by \( \mathcal{M} \) of (3.3) we obtain the equations
Thus the secular equation are, as we expected, reduced down to 2nd degrees. It is very simple problems to obtain the eigen-frequencies from (3.5).

(2) Diamond In the case of diamond which has two like C atoms in a unit cell, the treatment is different to (1), except the operation of translation. The translational matrix $M$ has the same type as (3.1) completely, and $(l, m, n)$ and $(l+1, m+1, n+1)$ are numbers which represent the coordinate of 2 like C atoms. From the view-point of translational operations, however, they can be treated as different atoms $a$ and $b$, because the two atoms are never interchanged by translation. Hereafter we denote atom of $a$ type, and $b$ type. Some calculation leads us to

$$
\Xi(k_x,k_y,k_z) = 
\begin{pmatrix}
A(k_x,k_y,k_z) & B(k_x,k_y) & C(k_x,k_y) & D(k_x,k_y) \\
B(k_x,k_y) & A(k_x,k_y) & D(k_x,k_y) & C(k_x,k_y) \\
B(k_x,k_y) & A(k_x,k_y) & D(k_x,k_y) & C(k_x,k_y) \\
C(k_x,k_y) & D(k_x,k_y) & C(k_x,k_y) & D(k_x,k_y)
\end{pmatrix}
$$

$$
A(k_x,k_y,k_z) = 2a + 4\beta - 2B\cos 2k_x(\cos k_y + \cos 2k_y),
B(k_x,k_y) = 2\beta \sin 2k_x \sin 2k_y,
C(k_x,k_y,k_z) = -a\{\cos(k_y + k_z)e^{ik_x} + \cos(k_y - k_z)e^{-ik_x}\},
D(k_x,k_y,k_z) = -a\{\cos(k_y + k_z)e^{ik_x} - \cos(k_y - k_z)e^{-ik_x}\},
$$

and $\bar{C}$, $\bar{D}$ are conjugate complex of $C$, $D$. 

The representation by the rotational operations are quite different from (1). For instance in the case of rotation $\pi/2$ about $z$ axis is

$$R_z(\pi/2)e_a(k_x, k_y, k_z; z) = \sum_{n} R_{b}(\pi/2) D^{k_z k_y k_x}_{mn} e_b(l, m, n; x)$$

$$= \sum_{b} D^{k_x k_y k_z}_{mn} e_b(-m, l, n; y) = \sum_{b} D^{k_x k_y k_z}_{mn} e_b(-m, l, n; y) = e(-k_y, k_x, k_z; y).$$

(3.7)

As the equation shows, the interchange of $a$ with $b$ often happens, and the representation by $K$-groups are not simple multiples of $(2\cdot 13), (2\cdot 14),$ and $(2\cdot 15)$. They are,

(1) $(k, k, k)$-group

<table>
<thead>
<tr>
<th>Element</th>
<th>$E$</th>
<th>$C_z(xy)$</th>
<th>$C_z^2(xy)$</th>
<th>$JC_z(x-y)$</th>
<th>$JC_z(x-z)$</th>
<th>$JC_z(y-z)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class</td>
<td>(1)</td>
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(3) \((k, 0, 0)\)-group

Element \(E\) \(\quad C_i^2(z)\) \(\quad C_i(x)\) \(\quad C_i^3(x)\)

Class \((1)\) \(\quad (2)\) \(\quad (3)\) \(\quad (3)\)

Rep. 

\[
\begin{pmatrix}
1 & 1 \\
1 & 1
\end{pmatrix}
\begin{pmatrix}
-1 & -1 \\
-1 & -1
\end{pmatrix}
\begin{pmatrix}
1 & -1 \\
-1 & 1
\end{pmatrix}
\begin{pmatrix}
1 & 1 \\
1 & 1
\end{pmatrix}
\]

\(JC_i^2(z)\) \(\quad JC_i^2(y)\) \(\quad JC_i(yz)\) \(\quad JC_i(y-2)\)

\[
\begin{pmatrix}
1 & -1 \\
1 & 1
\end{pmatrix}
\begin{pmatrix}
-1 & 1 \\
-1 & 1
\end{pmatrix}
\begin{pmatrix}
1 & -1 \\
1 & 1
\end{pmatrix}
\begin{pmatrix}
1 & 1 \\
1 & 1
\end{pmatrix}
\]

Res. \(A_1 + A_2^1 + 2A_0\) \(\quad (3 \cdot 10)\)

Trans. Mat. \(M(k, 0, 0)\)

\[
\begin{pmatrix}
1 & 1 & \cdots & \cdots & \cdots \\
\cdots & \cdots & 1 & 1 & \cdots \\
\cdots & \cdots & \cdots & 1 & 1 \\
1 & -1 & \cdots & \cdots & \cdots \\
\cdots & \cdots & 1 & -1 & \cdots \\
\cdots & \cdots & \cdots & 1 & -1
\end{pmatrix}
\]

The transformed matrix \(M^{-1} \otimes M\) have the following forms:

\[
\begin{pmatrix}
A + 2B & C + 2D \\
C + 2D & A + 2B
\end{pmatrix}, \quad \begin{pmatrix}
A^* - B & C - D \\
C - D & A^* - B
\end{pmatrix}
\]

\(A = 2\nu + A^*(\sin 2k)^2, \quad B = 2\beta (\sin 2k)^2\),

\(2\beta (\sin 2k)^2\),

\(A^* - B\)
Theory of the Normal Modes of Vibration in Crystal

\[ C = -u(\cos 2k e^{ik} + e^{-ik}), \quad D = -u(\cos 2k e^{ik} - e^{-ik}). \]

\[
\begin{pmatrix}
A + B + C + D & \sqrt{2} E \\
\sqrt{2} E & F - C
\end{pmatrix}, \quad
\begin{pmatrix}
A + B - C - D & \sqrt{2} E \\
\sqrt{2} E & F + C
\end{pmatrix},
\]

(3.12)

\[
\begin{pmatrix}
A - B - C + D \\
A - B + C - D
\end{pmatrix},
\]

\[
A = 2u + 4\beta - 2\beta \cos 2k (\cos 2k + 1), \quad B = 2\beta (\sin 2k)^2, \]

\[
C = -u(\cos 2k + 1), \quad D = u(1 - \cos 2k), \quad E = -iu \sin 2k,
\]

\[ F = 2u + 4\beta - 4\beta \cos 2k. \]

\[ A = 2u + 8\beta \sin^2 k, \quad B = 2u + 4\beta \sin^2 k, \quad C = -2u \cos k,
\]

\[ D = -2iu \sin k. \]

§ 4. Calculation of distribution functions of vibrational frequencies by Houston

Houston calculated the approximate distribution functions of the frequencies on a simple cubic crystal. We applied his method to more complex crystals. We calculated the frequencies applying our group theoretical method of reduction along the 3 directions in \( K \)-space.

For NaCl we solve the secular equation of (3.4), (3.5), and \( \mathfrak{D}(k,0,0) \), and represent the eigen-frequencies by the function of \( K \). The ratio of mass we assume for simplicity \( \mu : M = 1:2 \). Here \( Q \) is some constant times of eigen-frequencies. After some calculation, we have

\[
Q_1 = 1/2 \left\{ (3 + 1.2 \sin^2 k) \pm \left( (3 + 1.2 \sin^2 k)^2 - 4 (3.6 \sin^2 k + 0.32 \sin^4 k) \right)^{1/2} \right\},
\]

\[
Q_2 = 1/2 \left\{ (3 + 0.3 \sin^2 k) \pm \left( (3 + 0.3 \sin^2 k)^2 - 4 (2.4 \sin^2 k + 0.02 \sin^4 k) \right)^{1/2} \right\},
\]

\[
Q_3 = 1/2 \left\{ (3.6 - 0.6 \cos k) \pm \left( (3.6 - 0.6 \cos^2 k)^2 - 4 (0.88 - 0.96 \cos k + 0.08 \cos^2 k) \right)^{1/2} \right\},
\]

\[
Q_4 = 1/2 \left\{ (3.9 - 0.6 \cos^2 k - 0.3 \cos k) \pm \left( (3.9 - 0.6 \cos^2 k - 0.3 \cos k)^2 - 4 (3.38 - 0.52 \cos k - 0.52 \cos^2 k) \right)^{1/2} \right\},
\]

\[
Q_5 = 1/2 \left\{ (3.3 - 0.3 \cos k) \pm \left( (3.3 - 0.3 \cos k)^2 - 4 (2.42 - 0.44 \cos k - 1.98 \cos^2 k) \right)^{1/2} \right\},
\]

\[
Q_6 = 1/2 \left\{ (3.3 - 0.3 \cos k) \pm \left( (3.3 - 0.3 \cos k)^2 - 4 (0.02 \cos^2 k - 0.44 \cos k + 0.42) \right)^{1/2} \right\},
\]

\[
Q_7 = 1/2 \left\{ (3.6 - 0.6 \cos k) \pm \left( (3.6 - 0.6 \cos k)^2 - 4 (2.88 - 0.96 \cos k - 1.92 \cos^2 k) \right)^{1/2} \right\}.
\]

(4.1)

And similarly, for diamond, we have

\[
Q_1 = (4 + 0.8 \sin^2 2k) \pm 2(3 \cos^2 2k + 1)^{1/2},
\]

\[
Q_2 = 0.2 \sin^2 2k, \quad 0.2 \sin^2 2k + 8,
\]

(4.4)
\[ Q_3^2 = 0.4 \sin^2 \beta, \]
\[ Q_4^2 = 0.4 \sin^2 \beta + 8, \]
\[ Q_5^2 = (-0.2 \cos^2 2\beta + 1.3 \cos 2\beta + 5.5) \pm \left[ (-0.2 \cos^2 2\beta - 1.3 \cos 2\beta - 5.5)^2 \right]^{1/2}, \]
\[ Q_6^2 = (-0.2 \cos^2 2\beta + 0.7 \cos 2\beta + 3.5) \pm \left[ (-0.2 \cos^2 2\beta + 0.7 \cos 2\beta + 3.5)^2 \right]^{1/2}, \]
\[ Q_7^2 = -0.8 \cos^2 \beta - 4 \cos \beta + 4.8, \]
\[ Q_8^2 = -0.8 \cos^2 \beta + 4 \cos \beta + 4.8, \]
\[ Q_9^2 = \frac{1}{2} \left\{ (8.8 - 0.8 \cos^2 \beta) \pm \left[ (8.8 - 0.8 \cos^2 \beta)^2 \right]^{1/2} - 4 (4/25 \cos^2 \beta - 88/25 \cos^2 \beta + 84/25)^{1/2} \right\}. \]

Houston showed the approximate distribution functions are given by the equation.

\[ N(\nu) = \frac{4\pi}{280} \{ 89 F(\beta, 0, 0) + 92 F(\beta, \beta, 0) + 99 * F(\beta, \beta, \beta) \}. \]

After laborious numerical work, we obtained the distribution functions for NaCl and diamond as shown in Fig. (a) and (b).

The second order Raman effect in crystal are explained by superpositions of combination-tones and over-tones of ground frequencies calculated in \( K \)-space. We could obtain the similar distribution curves as Born and Bradburn did.

**Acknowledgments**

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**References**

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2) Houston, Rev. Mod. Phys. 29 (1948), 161.

* D. Nakamura pointed out that the coefficients of \( F(\beta, 0, 0) \) and \( F(\beta, \beta, 0) \) are mistake in the original calculations. The correct ones have been communicated privately by T. Nozawa and D. Nakamura to the author.