The theory of the Raman effect in crystals, in particular rock-salt

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The Raman effect in crystals is treated in this paper with the help of Placzek's approximation. It consists of contributions of different orders with respect to the amplitudes of the vibrations; the first-order effect is a line spectrum depending only on the vibrations of infinite wavelength, the second-order effect is a continuous spectrum depending on combination frequencies of all pairs of branches of the lattice vibrations, each pair taken for the same wave vector. In highly symmetrical crystals like rock-salt the first-order effect is zero. The second-order effect can be calculated for rock-salt with the help of the tables of the lattice frequencies published by Kellermann. It consists of thirty-six peaks, each belonging to a combination frequency. The superposition of these allows us to determine without any arbitrary assumption about the coupling constants, the frequency of the observable maxima in fair agreement with Krishnan's measurements. By adapting three coupling constants one can also determine the relative intensities of the most prominent peaks and obtain a curve which in its main features agrees with the observed one.

The results show that lattice dynamics can account quantitatively for the Raman effect in crystals and that Raman's attacks against the theory are unfounded.

INTRODUCTION

In the same year, 1928, as Raman discovered the existence of displaced lines in the light scattered by liquids, the Russian physicists, Landsberg and Mandelstam, found a similar phenomenon in crystals (quartz and calcite). The Raman effect provided a powerful tool for investigating the dynamical properties of molecules, and a detailed theory of molecular scattering in liquids and gases has been developed. Crystals have been comparatively neglected, and no systematic theory of their Raman effect seems to exist. The reason for this is easily understood. In those crystals which can be considered as composed of molecules the effect is roughly identical with that in the liquid state, simplified to some extent by the fixed orientation, but complicated by the coupling of the molecules; and as the main interest is directed towards using the Raman spectrum as a help to the chemist, the embedding of the molecule into a crystal appears as an unnecessary complication and nuisance. In atomic and ionic crystals, however, where the whole lattice has to be regarded as a single gigantic molecule, the intensity of the Raman effect is very often extremely small; for instance, when certain symmetry elements exist which produce a cancelling of terms of first order with respect to the vibrational amplitudes.

With the help of very long exposures, however, the second-order Raman effect can be observed. The first example of this kind was obtained by Rasetti (1931) and discussed by Fermi & Rasetti (1931). They found that the Raman effect in rock-salt crystals consists of a continuous background with peaks superimposed, and they developed the theory from the standpoint of ordinary lattice dynamics to a stage
where the continuous character of the spectrum could be understood; they abstained, however, from any attempt at a quantitative theory as their formulae were too involved.

We have now taken up this problem and developed the theory for rock-salt in some detail because Rasetti's observations have been used by Raman and his school as material for discrediting lattice dynamics and for proving their own strange theory of lattice vibrations. This theory contends that the vibrational spectrum is not quasi-continuous as correct classical or quantum mechanics implies, but consists of a small number of lines. All kinds of phenomena have been used by Raman for demonstrating this statement: specific heat, diffuse X-ray scattering, optical effects. The temperature dependence of the specific heat is, of course, not sensitive enough to supply a sharp criterion; it is, for example, well known that Lindemann's formula, which uses only two frequencies, can hardly be distinguished from Debye's formula, which uses a continuous spectrum. In the case of diffuse X-ray scattering the situation is now even less favourable for Raman's ideas; for it turns out that the diffuse thermal X-ray spots, when correctly interpreted, are a direct image of the continuous vibrational spectrum, which could in principle be derived from measurements of the intensity distribution of the scattering. There remains the optical effects, which, according to Raman, show directly the existence of only a small number of characteristic frequencies in crystals. Raman's pupil Krishnan (1943) has written a paper on the Raman effect in rock-salt, discussing and reinterpreting the observations of Fermi & Rasetti. He contends that their result has to be regarded as a line spectrum (of 9 Stokes and 9 anti-Stokes lines). Now the photograph of the spectrum may possibly be interpreted as a system of faint lines, though the continuous background seems obvious; Fermi & Rasetti have, however, published above the photograph the microphotometer curve of the intensity distribution which shows without the slightest doubt that the Italian authors are right in describing it as a continuum with small peaks. Krishnan says that the 9 lines, which he counts rather arbitrarily on each side of the incident line, are exactly what Raman's theory predicts; but he makes no attempt to calculate the position of the lines from his theory nor to discuss the intensities.

Recently, Krishnan (1945a) has repeated the observations and obtained a spectrum and microphotometer curve which is a confirmation of Rasetti's work and an improvement on it in so far as the little peaks are much sharper. Krishnan declares again that they constitute a line spectrum, but he counts only 6 strong and 2 weak lines, some of which may be double. So it seems that he has given up the claim that these peaks confirm the existence of 9 lines as predicted by Raman's theory.

Under these circumstances it seemed to us desirable to develop the correct lattice theory of the Raman effect for crystals and apply it quantitatively to rock-salt. This substance is particularly suited for this purpose, since Kellermann (1940) has published the theory of the lattice vibrations of rock-salt containing tables of the coefficients of the equations of motion and of the six frequency branches for a fairly narrow distribution of wave vectors.
We give here in §§ 1–5 the general theory for any crystal. The main result is that the second-order Raman effect is a continuous spectrum involving combinations \( \omega_J \pm \omega_J' \) of two frequencies in the same or different branches, but both belonging to the same wave vector. The peaks on this continuous background can be understood by a principle already used by Born & Blackman (1933) for explaining the fine structure of the residual rays (Reststrahlen), namely, that the density of the frequencies of a lattice has a maximum near the centre of the reciprocal cell. The Raman spectrum consists, in fact, of a number of steep and narrow continuous peaks which are superimposed in such a way that the observed aspect is obtained.

If this general theory is applied to rock-salt a satisfactory representation of the extent of the continuous background and the position of the main peaks is obtained; no arbitrary constants are introduced in the determination of these, as Kellermann’s results depend only on the measured lattice constant and compressibility of rock-salt. In order to explain the intensities the coupling constants between the ions of the lattice have to be adapted.

Krishnan has published some other second-order Raman effects, e.g. in diamond \( (1945b) \), obtained by extremely long exposures, which look superficially like faint lines. One can expect that these will also be explained quantitatively by a correct application of lattice dynamics.

1. The general theory of the Raman effect

A perfectly rigorous theory of crystal optics should proceed in this way: The quantized radiation field should be coupled to a set of nuclei and the corresponding number of electrons in an almost periodic array; the whole has to be treated as one quantum-mechanical system. This would, however, be extremely complicated. For the purpose of calculating the scattering the problem can be simplified by assuming the radiation enclosed in a very large box and the crystal small compared with the box, yet, on the other hand, large compared with the lattice cell. Then the whole crystal can be considered as one gigantic molecule and Dirac’s theory of the interaction between particles and radiation can be applied. The result can best be described by first considering the scattering classically.

Assume that the incident light is elliptically polarized,

\[
E = \Re(A e^{-i\omega t}) = \frac{1}{2}(A e^{-i\omega t} + A^* e^{i\omega t});
\]

it produces an electric moment \( \mathbf{M} \) with components

\[
M_\rho = \sum_\sigma \alpha_{\rho\sigma} A_\sigma \quad (\rho, \sigma = 1, 2, 3),
\]

† This theory was based on the assumption of non-harmonic terms in the potential energy. One can, however, explain the observations more simply without this assumption, using only harmonic vibrations, by taking into account the deformability of the particles. This will be shown in a separate publication.
where \( \alpha_{\rho\sigma} \) is the polarizability tensor. Let \( q \) be a unit vector normal to the direction of observation. The intensity of the light scattered in this direction is, apart from constant factors,

\[
I = \omega^{4} |M \cdot q|^{2} = \omega^{4} \sum_{\rho\sigma} \sum_{\mu\nu} \alpha_{\rho\sigma}^{\mu\nu} A_{\sigma}^{*} A_{\nu}^{*} q_{\rho} q_{\mu}.
\]  

(1.3)

In quantum theory the \( \alpha_{\rho\sigma} \) can be calculated in terms of the frequency \( \omega \) of the incident light, the energy levels of the scattering system and the matrix elements of its natural or unperturbed electric moment. The light scattered for the transition of the system from a quantum state \( n \) to another \( n' \) is obtained by replacing \( \alpha_{\rho\sigma} \) in formula (1.3) by the matrix element \( [\alpha_{\rho\sigma}]_{nn'} \) and \( \omega^{4} \) by \( (\omega + \omega_{nn'})^{4} \).

Practically only vibrational transitions are observable, producing the Rayleigh and Raman effect. In this case a simplification due to Placzek (1934) can be used. The polarizability \( \alpha \) can be calculated as if the nuclei were in fixed positions (neglecting their kinetic energy) so that it is a function of the nuclear configuration chosen, \( \alpha_{\rho\sigma}(X) \). Now if the nuclei are performing small vibrations \( (U) \) about equilibrium positions \( (X_{0}) \) so that \( X = X_{0} + U \), the vibrational states may be characterized by the quantum number \( v \) and the matrix elements of \( \alpha_{\rho\sigma}(U) \) with respect to \( v \), \( [\alpha_{\rho\sigma}]_{vv'} \), can be formed. Then (1.3) still holds for these coefficients. In this approximation \( (\omega + \omega_{nn'})^{4} \) can be neglected, as it is practically the same for all Raman lines of a given incident light:

\[
I_{vv'} = \sum_{\rho\sigma} \sum_{\mu\nu} [\alpha_{\rho\sigma}]_{vv'} [\alpha_{\rho\mu}]_{vv'} A_{\sigma}^{*} A_{\nu}^{*} q_{\rho} q_{\mu}.
\]

(1.4)

We shall specialize the general formulae for natural incident light and observations without an analyser. In this case the average over the azimuth of the polarization of the incident and scattered light has to be taken. If \( \theta_{\rho} \) \( (\rho = 1, 2, 3) \) are the angles between the incident beam and the co-ordinate axes and \( \phi_{\rho} \) \( (\rho = 1, 2, 3) \) those between the observed beam and these axes, an elementary consideration leads to

\[
\frac{A_{\rho} A_{\rho}^{*}}{q_{\rho} q_{\rho}} = -I_{0} \cos \theta_{\rho} \cos \theta_{\sigma} \quad (\rho \neq \sigma), \quad \frac{A_{\rho} A_{\rho}^{*}}{q_{\rho} q_{\rho}} = I_{0} \sin^{2} \theta_{\rho},
\]

where \( \theta_{0} = \frac{1}{2} |A|^{2} = E^{2} \) is the intensity of the incident light.

The problem is now reduced to the calculation of the quantities

\[
[i_{\rho\sigma, vv'}]_{vv'} = [\alpha_{\rho\sigma}]_{vv'} [\alpha_{\rho\mu}]_{vv'}
\]

(1.6)

for all vibrational transitions \( v \rightarrow v' \); but very many of these belong to the same frequency, particularly if the vibrations are considered to be harmonic (as we shall do in our case). Then the weighted mean of the quantity (1.6) has to be formed.

Let \( \epsilon_{v} \) be the energy in the state \( v \), then by multiplying by the Boltzmann factor the thermal average

\[
\langle i_{\rho\sigma, vv'} \rangle_{av} = \frac{\sum_{v} [i_{\rho\sigma, vv'}]_{vv'} e^{-\epsilon_{v}kT}}{\sum_{v} e^{-\epsilon_{v}kT}},
\]

(1.7)

where the summation is taken over the initial state \( v \). The result can be ordered with respect to the oscillator frequencies separating the state \( v' \) from the state \( v \).
Theory of Raman effect in crystals

2. Expansion of the polarizability

We describe the equilibrium of the crystal in the usual way with the help of the base index \( k \) and the cell index \((l_1, l_2, l_3)\). If \( n \) is the number of particles in the cell, \( k \) assumes \( n \) values 0, 1, 2, \( \ldots \), \( n - 1 \); if \( N \) is the number of cells the domain of \( l \) consists of \( N \) points. We denote by \( \mathbf{u}(l, k) \) a small displacement of the nucleus \((l, k)\) and write its three rectangular components \( u_\mu(l, k) (\mu = 1, 2, 3) \). The whole domain of values \( \mu, l, k \) is \( 3nN \).

The polarizability can then be expanded as a power series with respect to the \( u \),

\[
\alpha_{\rho\sigma} = \alpha_{\rho\sigma}^0 + \alpha_{\rho\sigma}^{(1)} + \alpha_{\rho\sigma}^{(2)} + \ldots
\]

where

\[
\alpha_{\rho\sigma}^0 = \text{constant},
\]

\[
\alpha_{\rho\sigma}^{(1)} = \sum_\mu \sum_{kl} \alpha_{\rho\sigma, \mu}(l, k) u_\mu(l, k),
\]

\[
\alpha_{\rho\sigma}^{(2)} = \sum_\mu \sum_{kl} \sum_{\mu'} \alpha_{\rho\sigma, \mu\mu'}(l, k, k', l', k') u_\mu(l, k) u_{\mu'}(l', k').
\]  

All these quantities are symmetric in \( \rho, \sigma \) but not in the other indices.

The coefficients satisfy a number of identities. The first set of these are consequences of the periodicity of the lattice. Any quantity which describes an equilibrium property and depends on only one single particle \((l, k)\) must be the same for all cells and hence independent of \( l \); in particular

\[
\alpha_{\rho\sigma, \mu}(l, k) \quad \text{independent of } l, = \alpha_{\rho\sigma, \mu}(k).
\]

Further, any equilibrium quantity depending on two points \((l, k)\) and \((l', k')\) is invariant if \( l \) and \( l' \) are subjected to the same cell displacement and hence depends only on the difference \( l - l' (l_1 - l'_1, l_2 - l'_2, l_3 - l'_3) \); in particular

\[
\alpha_{\rho\sigma, \mu}(l', k') = \alpha_{\rho\sigma, \mu}(l, k).
\]

A second set of identities is obtained from the consideration that any translation of the crystal as a whole does not change its electric moment. Hence if all \( \mathbf{u}(l, k) \) are taken equal (independent of \( l \) and \( k \)) \( \alpha_{\rho\sigma}^{(1)}, \alpha_{\rho\sigma}^{(2)} \) must vanish. Therefore

\[
\sum_k \alpha_{\rho\sigma, \mu}(k) = 0, \quad \sum_l \sum_{kk'} \alpha_{\rho\sigma, \mu}(l, k, k') = 0.
\]

3. Normal co-ordinates

As we have already said, we shall consider the vibrations to be harmonic. Let \( \Phi(X) \) be the total electronic energy for fixed nuclei which can be expanded with respect to the displacements \( U \) in the neighbourhood of the equilibrium position \( X_0 \),

\[
\Phi(X) = \Phi(X_0 + U) = \Phi_0 + \Phi_1 + \Phi_2 + \ldots,
\]
where $\Phi_r$ is of degree $r$ in $U$. $\Phi_1$ vanishes in equilibrium. $\Phi_2$ can be written

$$\Phi_2 = \frac{1}{h} \sum_{\mu \nu} \sum_{k l} \Phi_{\mu \nu} \begin{pmatrix} l - l' \\ kk' \end{pmatrix} u_\mu \begin{pmatrix} l \\ k \end{pmatrix} u_\nu \begin{pmatrix} l' \\ k' \end{pmatrix}, \quad (3.2)$$

where the coefficients are the equilibrium values of the second derivatives,

$$\frac{\partial^2 \Phi}{\partial u_\mu \begin{pmatrix} l \\ k \end{pmatrix} \partial u_\nu \begin{pmatrix} l' \\ k' \end{pmatrix}} = \Phi_{\mu \nu} \begin{pmatrix} l - l' \\ kk' \end{pmatrix} = \sqrt{(m_k m_{k'}) D_{\mu \nu} \begin{pmatrix} l - l' \\ kk' \end{pmatrix}}, \quad (3.3)$$

which depend on two points and therefore on the difference $l - l'$ only. $D$ considered as a function of the two sets of indices $\mu, l$, $k$ and $\nu, l'$, $k'$ is called the dynamical matrix.

Now the quantum theory of electronic systems (Born & Oppenheimer 1927) shows that the total electronic energy can be considered to be the potential energy for the motion of the nuclei. Their kinetic energy is

$$\mathcal{T} = \frac{1}{2} \sum_{\mu l} m_k \dot{u}_k \begin{pmatrix} l \\ k \end{pmatrix}^2. \quad (3.4)$$

Now introduce normal co-ordinates with the help of which $\Phi_2$ and $\mathcal{T}$ are transformed into the sums of squares. We give only the results of the well-known method. Let $\xi(J)$ be complex normal co-ordinates where the index $J$ assumes the same number of values $3nN$ as the domains of $\mu$, $k$, $l$ together. Then one has

$$\sqrt{(m_k)} u_\mu \begin{pmatrix} l \\ k \end{pmatrix} = \sum_J \varepsilon_{\mu} \begin{pmatrix} l \\ k \end{pmatrix} J \xi(J),$$

$$\xi(J) = \sum_{\mu, l, k} \varepsilon^*_{\mu} \begin{pmatrix} l \\ k \end{pmatrix} \sqrt{(m_k)} u_\mu \begin{pmatrix} l \\ k \end{pmatrix}. \quad (3.5)$$

The coefficients are the solutions of the linear equations for free vibrations (waves). In consequence of the periodicity of the lattice these can be split into $N$ sets of $3n$ equations,

$$\omega_j^2 \begin{pmatrix} Q \\ j \end{pmatrix} \mu \begin{pmatrix} k \\ j \end{pmatrix} = \sum_{\nu} \sum_{k'} D_{\mu \nu} (kk' | Q) \varepsilon_{\nu} \begin{pmatrix} k' \\ j \end{pmatrix}, \quad (3.6)$$

where

$$D_{\mu \nu} (kk' | Q) = \sum_l D_{\mu \nu} \begin{pmatrix} l \\ kk' \end{pmatrix} e^{-2\pi it(Q, k)}, \quad (l, Q) = l_1 Q_1 + l_2 Q_2 + l_3 Q_3. \quad (3.7)$$

Since obviously

$$D_{\mu \nu} (kk' | -Q) = D^*_{\nu \mu} (kk' \mid Q), \quad (3.8)$$

it follows that

$$\varepsilon_{\mu} \begin{pmatrix} k \mid -Q \end{pmatrix} = \varepsilon^*_{\mu} \begin{pmatrix} k \mid Q \end{pmatrix}. \quad (3.9)$$

The index $J$ has been split into two indices $\begin{pmatrix} Q \\ j \end{pmatrix}$, where $j = 1, 2, \ldots, 3n$ represents the different branches of the spectrum and $Q(Q_1, Q_2, Q_3)$ the different waves of each branch. The full set of different values of $Q$ is represented by the points which are obtained on dividing any unit cell in reciprocal space into $N = L^3$ sub-cells each of side $1/L$. 

166 M. Born and M. Bradburn
Theory of Raman effect in crystals

The coefficients in (3·5) are the elements of a unitary matrix and can be written

\[ e_\mu \left( \begin{array}{c} l \\ k \end{array} \right) = e_\mu \left( \begin{array}{c} l \\ Q \end{array} \right) = e_\mu \left( \begin{array}{c} k \\ Q \end{array} \right) e^{2\pi i l(Q_k) Q}, \]  

(3·10)

where the \( e_\mu \left( \begin{array}{c} k \\ Q \end{array} \right) \) must satisfy the identities

\[ \sum_{\mu, k} e_\mu \left( \begin{array}{c} k \\ Q \end{array} \right) e_\mu^* \left( \begin{array}{c} k' \\ Q \end{array} \right) = \delta(jj'), \quad \sum_j e_\mu \left( \begin{array}{c} Q \\ j \end{array} \right) e_\mu^* \left( \begin{array}{c} Q \\ j' \end{array} \right) = \delta(j\mu) \delta(kk'). \]  

(3·11)

Since the \( u \left( \begin{array}{c} l \\ k \end{array} \right) \) are real, one has

\[ \xi \left( \begin{array}{c} -Q \\ j \end{array} \right) = \xi^* \left( \begin{array}{c} Q \\ j \end{array} \right). \]  

(3·12)

Now each complex \( \xi \) represents two real normal co-ordinates, but on account of (3·12) the number of these can be reduced to the proper value again by restricting the \( Q \) values to half the points in the unit cell of reciprocal space.

4. Expression of polarizability in terms of normal co-ordinates

Substituting (3·5) in (2·2) one obtains

\[ \alpha_{\mu'\nu'}^{(l)} = \sum_k \sum_{\mu, \rho, \sigma} \alpha_{\rho, \sigma, \mu}(k) u_{\mu} \left( \begin{array}{c} l \\ k \end{array} \right) \]  

\[ = \sum_{Qj} \sum_k \sum_{\mu, \rho, \sigma} \alpha_{\rho, \sigma, \mu}(k) e^{2\pi i l(Q_k) Q} e_\mu \left( \begin{array}{c} k \\ Q \end{array} \right) \xi \left( \begin{array}{c} Q \\ j \end{array} \right) \frac{1}{\sqrt{m_k}}. \]  

(4·1)

Here the factor \( \sum_l e^{2\pi i l(Q_k) Q} \) splits off; it is a \( \delta \)-function vanishing except for \( Q = 0 \).

Hence

\[ \alpha_{\mu'\nu'}^{(l)} = \sum_j \sum_k \sum_{\mu, \rho, \sigma} \alpha_{\rho, \sigma, \mu}(k) e_\mu \left( \begin{array}{c} k \\ 0 \end{array} \right) \xi \left( \begin{array}{c} 0 \\ j \end{array} \right) \frac{1}{\sqrt{m_k}}. \]  

(4·2)

The first-order Raman effect is therefore due only to vibrations with wave number zero or infinite wave-length, where each of the \( n \) simple lattices corresponding to the \( n \) points of the base moves like a rigid system. The matrix elements \( \left[ \xi \left( \begin{array}{c} 0 \\ j \end{array} \right) \right]_{\nu'\nu} \) vanish except for transitions belonging to the frequencies \( \pm \omega \left( \begin{array}{c} 0 \\ j \end{array} \right) \); therefore the first-order Raman effect is a line spectrum of not more than \( 3n - 3 \) lines (as the three acoustical branches have \( \omega \left( \begin{array}{c} 0 \\ j \end{array} \right) = 0 \)), each line corresponding to a normal mode of the system of \( n \) interpenetrating rigid simple lattices. It is the same as the Raman effect of a molecule of \( n \) particles, with a fixed orientation in space (translations allowed, rotations excluded) having the dynamical matrix (3·7)

\[ \mathcal{D}_{\mu'(kk') \mu(k)} = \sum_{\mu'} \mathcal{D}_{\mu'} \left( \begin{array}{c} l \\ kk' \end{array} \right). \]
But (4·2) always vanishes if each lattice point is a centre of symmetry. This is the case in many simple crystals, among them rock-salt. Therefore we shall not discuss the first-order Raman effect any further.

In the same way it follows from (2·2) and (3·5) that

\[
\alpha_{\rho\sigma}^{(2)} = \sum_{l\mu} \sum_{k \neq k'} \alpha_{\rho\sigma, \mu \nu}(l-l') u_{\mu}(l) u_{\nu}(l')
\]

\[
= \sum_{Qj} \sum_{Qj'} \sum_{l \neq k \neq k'} \alpha_{\rho\sigma, \mu \nu}(l-l') \frac{e^{2\pi iQl}}{4\pi} e_{\mu}(l) e_{\nu}(l') \frac{\xi(Q)_j}{\sqrt{(m_k m_{k'})}} \frac{\xi(Q')_{j'}}{\sqrt{(m_k m_{k'})}}.
\]

Replacing \(l-l'\) by \(l\) the factor \(e^{2\pi iQl}\) splits off; it is a \(\delta\)-function of \(Q+Q'\), hence in the sum (4·3) only the terms \(Q' = -Q\) appear. Using (3·5) and (3·9)

\[
\alpha_{\rho\sigma}^{(2)} = \sum_{Qj} \sum_{Qj'} \alpha_{\rho\sigma}(Q_{jj'}) \xi(Q_j) \xi(Q_{j'})^*,
\]

where

\[
\alpha_{\rho\sigma}(Q_{jj'}) = \sum_{l \neq k \neq k'} \alpha_{\rho\sigma, \mu \nu}(l) e^{2\pi iQl} e_{\mu}(l) e_{\nu}(l') \frac{\xi(Q_j)}{\sqrt{(m_k m_{k'})}} \frac{\xi(Q_{j'})}{\sqrt{(m_k m_{k'})}}.
\]

5. THERMAL AVERAGES AND THE INTENSITY DISTRIBUTION

Now substitute (4·4) for \(\alpha_{\rho\sigma}^{(2)}\) in (1·6) giving

\[
[i_{\rho\sigma, \mu \nu}]_{v'v} = \sum_{Qj} \sum_{Qj'} \alpha_{\rho\sigma}(Q_{jj'}) \xi(Q_j) \xi(Q_{j'})^* \sum_{Q'j''} \sum_{Q'j'''} \alpha_{\rho\sigma}(Q'_{jj'}) \xi(Q'_{j''}) \xi(Q'_{j'''}^*) \sum_{Q'j''} \sum_{Q'j'''} \alpha_{\rho\sigma}(Q'_{jj'}) \xi(Q'_{j''}) \xi(Q'_{j'''}^*) \xi(Q_j) \xi(Q_{j'})^* \xi(Q_{j'_{j''}^*}) \xi(Q_{j'''}^*).
\]

This expression is then to be inserted in (1·7) and the result will obviously be a sum of terms of the type

\[
\langle \xi(Q_j) \xi(Q_{j'})^* \xi(Q'_{j''}) \xi(Q'_{j'''}^*) \rangle_{v'v}.
\]

The quantum number \(v\) represents the set \(v_1, v_2, v_3, \ldots\) of the quantum numbers of the single oscillators.

It is well known that the matrix elements \(\eta_{ij}\) of the amplitude \(\eta_{ij}\) of one of a set of real oscillators vanish except when \(v_{ij}\) changes by \(\pm 1\) while all other \(v_{ij}\) are unchanged. The matrix elements of the square \(\eta_{ij}^2\) vanish except when \(v_{ij}\) changes by \(0, \pm 2\) and those of the product \(\eta_{ij} \eta_{ij'} (J+J')\), except when \(v_{ij}\) and \(v_{ij'}\) change simultaneously by \(\pm 1\).

The results can be ordered according to the frequencies

\[
o_{v'v} = \sum_J o(J) (v_{ij} - v_{ij'},
\]

and are given in table 1, where \(c_J = \sqrt[3]{[\hbar/2o(J)]}\).
Theory of Raman effect in crystals

Table 1

\[
\begin{array}{ccc}
\eta J & \eta J & -2\omega(J) \\
\hline
\eta J & c_0(2v_J + 1) & c_0^2[(v_J + 1)(v_J + 2)] \\
\eta^2 & - & c_0^2[v_J(v_J - 1)] \\
\eta J & c_Jc_J\sqrt{(v_J + 1)(v_J + 1)} & c_Jc_J\sqrt{v_Jv_J} \\
\eta^2 & - & c_Jc_J\sqrt{v_J(v_J + 1)}
\end{array}
\]

A product of the form \((5\cdot2)\) with real oscillators, e.g.

\[
\langle [\eta J, \eta J]_{\nu\nu'} [\eta J, \eta J]_{\nu\nu'} \rangle_{av}
\]

(5.4)

where the two factors refer to the same transition \(v \rightarrow v'\), is obviously zero except when the first factor refers to the same two oscillators as the second, i.e. if either

\[
J = J'' , J' = J''' \text{ or } J = J''' , J' = J'' .
\]

(5.5)

Now consider a system of complex oscillators

\[
\xi(J) = \eta + i\zeta ,
\]

(5.6)

where \(\eta\) is short for \(\eta_J\), then the last result still applies.

Consider first \(J = J' = J''' = J''\), then

\[
\langle [\xi(J) \xi^*(J)]_{\nu\nu'} [\xi^*(J) \xi(J)]_{\nu\nu'} \rangle_{av} = \langle [\xi \xi^*]_{\nu\nu'} \rangle_{av}
\]

(5.7)

where we have omitted the argument \(J\). Now consider only transitions \(v \rightarrow v'\) corresponding to the Raman effect (not the Rayleigh effect, i.e. excluding \(v' = v\)). Then

\[
\langle [\xi \xi^*]_{\nu\nu'} \rangle_{av} = \langle [\eta^2]_{\nu\nu'} + [\zeta^2]_{\nu\nu'} + 2[\eta \zeta]_{\nu\nu'} [\zeta^2]_{\nu\nu'} \rangle_{av}.
\]

(5.8)

Here the last term vanishes; for the meaning of the brackets is explicitly the following:

\[
[\eta^2]_{\nu\nu'} = [\eta^2]_{n,n\pm 2} \delta(n,n' + 2) \delta(m,m'),
\]

\[
[\zeta^2]_{\nu\nu'} = [\zeta^2]_{m,m\pm 2} \delta(n,n') \delta(m,m' + 2),
\]

(5.9)

where \(n\) is the quantum number belonging to \(\eta\), \(m\) that belonging to \(\zeta\), and \(v' + v\). Hence the product vanishes. Since, however, the two matrix elements which appear in the other terms belong to the same transition frequency, (5.8) finally reduces to

\[
\langle [\xi \xi^*]_{\nu\nu'} \rangle_{av} = 2\langle [\eta^2]_{\nu\nu'} \rangle_{av}.
\]

(5.10)

In the same way, if \(J = J''\), \(J' = J'''\), \(J \neq J'\),

\[
\langle [\xi(J) \xi^*(J')]_{\nu\nu'} [\xi^*(J') \xi(J)]_{\nu\nu'} \rangle_{av} = \langle [\eta \eta^*]_{\nu\nu'} + [\zeta \zeta^*]_{\nu\nu'} + [\eta \zeta]_{\nu\nu'} [\zeta^2]_{\nu\nu'} \rangle_{av}
\]

\[
= 4\langle [\eta \eta^*]_{\nu\nu'} \rangle_{av},
\]

(5.11)

and in the third case \(J = J'''\), \(J' = J''\); \(J \neq J'\),

\[
\langle [\xi(J) \xi^*(J')]_{\nu\nu'} [\xi(J) \xi^*(J')]_{\nu\nu'} \rangle_{av} = \langle [\eta \eta^*]_{\nu\nu'} + [\zeta \zeta^*]_{\nu\nu'} - [\eta \zeta]_{\nu\nu'} [\zeta^2]_{\nu\nu'} \rangle_{av}
\]

\[
= 0.
\]

(5.12)
Finally, the averages for the real oscillators occurring in the formulae (5.10) and (5.11) have to be calculated. With the abbreviation
\[ \beta(J) = \frac{\hbar \omega(J)}{kT}, \quad \langle J \rangle = \frac{c_J^3}{1 - e^{-\beta(J)}}, \quad (5.13) \]
straightforward calculations from (1.7) and table 1 lead to the results shown in table 2.

<table>
<thead>
<tr>
<th>(2\omega(J))</th>
<th>(2\langle J \rangle^2 e^{-2\beta(J)})</th>
<th>(2\langle J \rangle^2)</th>
<th>(\omega(J) + \omega(J'))</th>
<th>(\omega(J) - \omega(J'))</th>
<th>(\omega(J') - \omega(J))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\langle [\eta^2_{ij}]<em>{\nu\nu} \rangle</em>{av})</td>
<td>(\langle [\eta^2_{ij}]<em>{\nu\nu} \rangle</em>{av})</td>
<td>(\langle [\eta^2_{ij}]<em>{\nu\nu} \rangle</em>{av})</td>
<td>(\langle [\eta^2_{ij}]<em>{\nu\nu} \rangle</em>{av})</td>
<td>(\langle [\eta^2_{ij}]<em>{\nu\nu} \rangle</em>{av})</td>
<td>(\langle [\eta^2_{ij}]<em>{\nu\nu} \rangle</em>{av})</td>
</tr>
</tbody>
</table>

The intensities corresponding to these six frequencies are obtained from (5.1) with the help of (5.10), (5.11) and (5.12). Writing
\[ \omega(Q_{jj'}) = \omega(Q_{jj'}) + \omega(Q_{jj'}'), \]
the Stokes lines (St.) correspond to the frequency shift \(\omega(Q_{jj'})\) and the anti-Stokes (A.St.) to \(\omega(Q_{jj'})\). The frequencies and the intensities of single emissions are given by the following scheme:

\[ \omega(Q_{jj'}) = \left\{ \begin{array}{l} \omega(Q_{jj'}) + \omega(Q_{jj'}) \\
\omega(Q_{jj'}) - \omega(Q_{jj'}) \end{array} \right\} \times_{\rho r, \rho s}(Q_{jj'}) = 2\langle J \rangle \langle J' \rangle \alpha_{\rho r}(Q_{jj'}) \alpha_{\rho s, \rho s}(Q_{jj'}) \]

St. \quad A.St.
\[
+ \alpha_{\rho r}(Q_{jj'}) \alpha_{\rho s, \rho s}(Q_{jj'}) \left\{ \begin{array}{l} 1 \\
\exp[-\beta(Q_{jj'})] \end{array} \right\} \left\{ \begin{array}{l} \exp[-\beta(Q_{jj'})] \\
\exp[-\beta(Q_{jj'})] \end{array} \right\}.
\]

To obtain the observed intensities one must first integrate over that part of the reciprocal space \(Q\) which belongs to a frequency \(\omega\), i.e.

\[ i_{\rho r, \rho s}(\omega) d\omega = \sum_{\rho r, \rho s} \int_{\omega} \int_{|\omega' - \omega|} i_{\rho r, \rho s}(Q_{jj'}) dQ_1 dQ_2 dQ_3, \quad (5.15) \]

where the Stokes and anti-Stokes lines have to be taken separately. Then the total intensity for a given incident beam \(A\) and a given position of the analyser \(q\) is, from (1.4),

\[ I(\omega) = \sum_{\rho r, \rho s} i_{\rho r, \rho s}(\omega) A_{\rho r} A_{\rho s}^* q_{\rho} q_{\rho}, \quad (5.16) \]
Theory of Raman effect in crystals

The number of terms in the sum (5.15) over \( j \) and \( j' \) is \((3n)^2\); for instance, for a diatomic base it is 36. Hence the whole observable spectrum consists of \(9n^2\) superimposed continuous bands each of which will have a maximum at a certain point. This result explains at once the general feature of the observed spectrum; that it consists of a continuous background with a considerable number of peaks.

We shall not continue the general theory any further except to indicate a few points in the evaluation of the intensity. Symmetry considerations can be used to simplify the \( \alpha \)-factors occurring in (5.14) using the explicit expressions (4.5). This would be extremely involved if it were to be done for all waves, i.e. for all points of the reciprocal space \( Q \). In fact, the integral (5.15) will depend very little on the whole distribution of \( i_{\rho \sigma, \mu \nu}(Q, j_j) \) in the \( Q \)-space, but mainly on those parts where the frequencies have a maximum of density. The general problem of finding these regions of the \( Q \)-space would also be very involved (we shall solve it approximately in the special case of rock-salt). If it is solved it would suffice to apply the symmetry considerations to these special waves which would be a much simpler problem than the general one and would lead to a classification of the qualitative feature of the Raman spectra of crystals according to the symmetry of the lattice.

6. Raman effect in rock-salt

For the rock-salt lattice the whole vibration spectrum has been calculated by Kellermann (1940) for a set of \( Q \)-values sufficiently complete to get a good idea of all the branches. His assumptions are Coulomb forces acting between all ions and repulsive forces between next neighbours; the two constants appearing from the latter can be calculated by using the experimental values of the lattice constant and the compressibility. Hence his results are independent of arbitrary assumptions, and they are checked by the calculations of the specific heat (Kellermann 1941).

First consider the factor containing the polarizability \( \alpha \) in (5.14), assuming that the constants \( \alpha_{\rho \sigma, \mu \nu}(l_{kk'}) \) in (4.5) are different from zero only for next neighbours; even under this simplified assumption seven independent constants appear. For rock-salt, a diatomic cubic crystal, \( k \) and \( k' \), are equal to either 1 or 2, and there are six next neighbours:

\[
\begin{array}{ccccccc}
l & 1 & 2 & 3 & 4 & 5 & 6 \\
l_1 & 1 & 0 & 0 & -1 & 0 & 0 \\
l_2 & 0 & 1 & 0 & 0 & -1 & 0 \\
l_3 & 0 & 0 & 1 & 0 & 0 & -1 \\
\end{array}
\]

From general symmetry considerations

\[
\alpha_{\rho \sigma, \mu \nu}(l_{kk'}) = \alpha_{\rho \sigma, \mu \nu}(-l_{k'k}),
\]

(6.1)
and since any lattice point of rock-salt is a centre of symmetry

\[ \alpha_{\rho \sigma, \mu \nu} \left( \frac{l}{kk'} \right) = \alpha_{\rho \sigma, \mu \nu} \left( \frac{-l}{kk'} \right), \]  

(6.2)

The following equations give the seven essential non-zero \( \alpha_{\rho \sigma, \mu \nu} \left( \frac{l}{kk'} \right) \):

\[
\begin{align*}
\alpha_{11, 11} \left( \frac{1}{12} \right) &= a, \\
\alpha_{22, 22} \left( \frac{1}{12} \right) &= \alpha_{33, 33} \left( \frac{1}{12} \right) = b, \\
\alpha_{22, 33} \left( \frac{1}{12} \right) &= \alpha_{33, 22} \left( \frac{1}{12} \right) = c, \\
\alpha_{11, 22} \left( \frac{1}{12} \right) &= \alpha_{11, 33} \left( \frac{1}{12} \right) = \alpha_{22, 11} \left( \frac{1}{12} \right) = \alpha_{33, 11} \left( \frac{1}{12} \right) = d, \\
\alpha_{23, 23} \left( \frac{1}{12} \right) &= \alpha_{32, 32} \left( \frac{1}{12} \right) = e, \\
\alpha_{31, 31} \left( \frac{1}{12} \right) &= \alpha_{21, 21} \left( \frac{1}{12} \right) = f, \\
\alpha_{12, 12} \left( \frac{1}{12} \right) &= \alpha_{13, 13} \left( \frac{1}{12} \right) = g.
\end{align*}
\]

(6.3)

Those \( \alpha_{\rho \sigma, \mu \nu} \left( \frac{l}{kk'} \right) \) which are obtained by interchanging the 2 and 3 axes have been written out in full; all others may be obtained by the use of equations (6.1), (6.2) and (2.5) and by cyclic interchange of the axes.

The \( \alpha \left( \frac{Q}{jj'} \right) \) from (4.5) have now to be calculated. For this purpose the whole set of eigenvectors \( e_{\rho} (k | Q \rangle \langle j) \) should be known. These are not given by Kellermann, and even if they were, the calculations for all points in the \( Q \) space would be much too complicated. Now as we have remarked before the integral (5.15) depends essentially on those points of the \( Q \)-space where the density of frequency is a maximum. For a linear lattice it can be said that this is the case at the centre point of the cell in reciprocal space. In the three-dimensional case the density \( z_{jj'} (\omega) \) of the frequency \( \omega \left( \frac{Q}{jj'} \right) \) is defined by the integral

\[
z_{jj'} (\omega) d\omega = \int \int \int_{\omega = \omega \left( \frac{Q}{jj'} \right)} \omega dQ_1 dQ_2 dQ_3.
\]

(6.4)

The functions \( \omega \left( \frac{Q}{jj'} \right) \) are stationary at the centre of the reciprocal cell, \( Q = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \);
Theory of Raman effect in crystals

hence no great error will arise if this value of $Q$ be taken in calculating the $\alpha_{\rho\sigma}(Q)$ and the other factors in (5·14). This means that using this approximation (5·15) is replaced by

$$i_{\rho\sigma,\mu\nu}(\omega) = \sum_{jj'} i_{\rho\sigma,\mu\nu}(jj') z_{j'j}(\omega),$$  \hspace{1cm} (6·5)

where $(jj')$ now refers to $\binom{Q}{j'j}$ for the point $Q = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$.

Then the total intensity is

$$I(\omega) = \sum_{\rho\sigma} \sum_{\mu\nu} i_{\rho\sigma,\mu\nu}(\omega) A_\rho^{*} A_\mu^{*} q_\sigma q_\nu,$$  \hspace{1cm} (6·6)

Now consider the case where an unpolarized incident beam along a crystal axis is observed normal to its direction without analyser. Using the formula (1·5) we have put $\theta_1 = 0$, $\theta_2 = \theta_3 = \frac{1}{2}\pi$ and $\phi_1 = \phi_2 = \phi_3 = \frac{1}{2}\pi$. Then

$$\begin{align*}
A_\rho^{*} A_\sigma^{*} = 0, & \quad q_\rho q_\sigma = 0; \quad \rho \neq \sigma, \\
A_1 A_1^{*} = 0; & \quad A_2 A_2^{*} = A_3 A_3^{*} = I_0,
\end{align*}$$  \hspace{1cm} (6·7)

giving from (6·6)

$$I(\omega) = \frac{1}{2} I_0 \{ i_{23,23}(\omega) + i_{31,31}(\omega) + i_{12,12}(\omega) + i_{33,33}(\omega) \}. \hspace{1cm} (6·8)$$

The first three terms are cyclic in the three indices and therefore represent an isotropic behaviour. The last term depends on the axis normal to the plane of the incident and observed light and represents anisotropy around the incident beam. This effect is neglected and $i_{33,33}(\omega)$ is replaced by $\frac{1}{4} \sum_{\rho} i_{\rho\rho,\rho\rho}(\omega)$, which is a reasonable approximation for cubic crystals. Hence using the fact that in (6·8) the pair $\rho\sigma$ is always the same as the pair $\mu\nu$, then

$$A(jj') = \frac{1}{2} \sum_{\rho\mu} |\alpha_{\mu\nu}(jj')|^2 + \frac{1}{2} \sum_{\rho\mu} |\alpha_{\rho\mu}(jj')|^2$$  \hspace{1cm} (6·9)

must be evaluated.

A lengthy calculation gives the sums (4·5) at the point $Q = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$:

$$\begin{align*}
\alpha_{11}(jj') &= -2F \left( \frac{1}{m_1} e_1(1 | j) e_1^{*}(1 | j') + \frac{1}{m_2} e_1(2 | j) e_1^{*}(2 | j') \right) \\
&\quad - 2G \left[ \frac{1}{m_1} [e_2(1 | j) e_2^{*}(1 | j') + e_3(1 | j) e_3^{*}(1 | j')] \right. \\
&\quad \left. + \frac{1}{m_2} [e_2(2 | j) e_2^{*}(2 | j') + e_3(2 | j) e_3^{*}(2 | j')] \right], \\
\alpha_{33}(jj') &= -2H \left( \frac{1}{m_1} [e_2(1 | j) e_2^{*}(1 | j') + e_3(1 | j) e_3^{*}(1 | j')] \right. \\
&\quad \left. + \frac{1}{m_2} [e_2(2 | j) e_2^{*}(2 | j') + e_3(2 | j) e_3^{*}(2 | j')] \right), \\
\end{align*}$$  \hspace{1cm} (6·10)

where the constants of (6·3) can now be replaced by three constants

$$F = a + 2b, \quad G = c + 2d, \quad H = e + f + g.$$  \hspace{1cm} (6·11)
These three constants determine the intensities of the second-order Raman effect. They are the only arbitrary factors in the expression (6.8) for \( I(\omega) \), and are the only quantities which have been adapted to fit the measurements.

In order to evaluate \( e_\rho(k \mid j) \) equations of motion must be established at \( Q = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \). It can be shown by simple symmetry considerations, as in Kellermann (1940), that the six equations (3.6) split into two sets of three. The first equation of either set is of the form

\[
(A - m_k \omega^2) e_1(k \mid j) + B [e_2(k \mid j) + e_3(k \mid j)] = 0, \tag{6.12}
\]

with two others obtained by cyclic interchange of the suffix \( \rho \) of \( e_\rho(k \mid j) \). The two sets are distinguished by \( k = 1 \) or \( 2 \). The values of \( j \) shall be chosen to correspond with Kellermann’s notation. With the help of the orthogonality relations (3.11) the solutions of these equations are

\[
\begin{align*}
    j = 1: & \quad m_1 \omega^2(1) = A + 2B; \quad e_1(1 \mid j) = e_2(1 \mid j) = e_3(1 \mid j) = \frac{1}{\sqrt{3}}; \\
    e_1(2 \mid j) &= e_2(2 \mid j) = e_3(2 \mid j) = 0; \\
    j = 2: & \quad m_2 \omega^2(2) = A + 2B; \quad e_1(1 \mid j) = e_2(1 \mid j) = e_3(1 \mid j) = 0; \\
    e_1(2 \mid j) &= e_2(2 \mid j) = e_3(2 \mid j) = \frac{1}{\sqrt{3}}; \\
    j = 3 \text{ or } 4: & \quad m_1 \omega^2(3) = m_1 \omega^2(4) = A - B; \quad e_1(1 \mid j) + e_2(1 \mid j) + e_3(1 \mid j) = 0; \\
    e_1(2 \mid j) = e_2(2 \mid j) = e_3(2 \mid j) = 0. \\
    j = 5 \text{ or } 6: & \quad m_2 \omega^2(5) = m_2 \omega^2(6) = A - B; \quad e_1(1 \mid j) = e_2(1 \mid j) = e_3(1 \mid j) = 0; \\
    e_1(2 \mid j) + e_2(2 \mid j) + e_3(2 \mid j) = 0; \\
    e_1(2 \mid j) + e_2(2 \mid j) + e_3(2 \mid j) = 1. 
\end{align*}
\tag{6.13}
\]

Using equations (6.10) in (6.9) and substituting the above values of \( e_\rho(k \mid j) \) after some calculations the following values of \( A(jj') \) are found:

\[
\begin{align*}
    j = j' = 1: & \quad A(11) = \frac{4}{3m_1^2} [\frac{1}{3} (F + 2G)^2 + 4H^2], \\
    j = j' = 3 \text{ or } 4: & \quad A(33) = A(44) = \frac{4}{3m_1^2} [\frac{1}{12} (F^2 + 2FG + 3G^2) + \frac{3}{2} H^2], \\
    j = 1, j' = 3 \text{ or } 4: & \quad A(13) = A(14) = \frac{4}{3m_1^2} [\frac{1}{3} (F - G)^2 + H^2], \\
    j = 3, j' = 4: & \quad A(34) = \frac{1}{2} A(13). 
\end{align*}
\tag{6.14}
\]

The \( A(jj') \) for the \( j = 2, 5 \) or 6 group are found by replacing \( m_1 \) by \( m_2 \). If \( j \) belongs to the \( (1, 3, 4) \) group and \( j' \) to the \( (2, 5, 6) \), it can be seen from (6.13) that all products \( e_\rho(k \mid j) e_\sigma^*(k \mid j') \) are zero; so the corresponding \( A(jj') \) is zero.
Theory of Raman effect in crystals

Combining these results it is found that the approximation to the intensity distribution is

\[
I(\omega) = \frac{1}{2} I_0 \sum_{jj'} z_{jj'}(\omega) \mathcal{C}_j \mathcal{C}_{j'} A(jj') \left\{ \begin{array}{l}
1 \\
\frac{1}{e^{-\beta_j} - 1} e^{-\beta_j}
\end{array} \right.
\]

where \( \mathcal{C}_j \) and \( \beta_j \) are taken at the point \( Q = (\frac{1}{3}, \frac{1}{3}, \frac{1}{3}) \).

7. Numerical calculations

First calculate the density \( z_{jj'}(\omega) \) for each pair of branches. Kellermann gives a table of frequencies of each branch from which \( \omega \left( \frac{Q}{j} \right) \pm \omega \left( \frac{Q}{j'} \right) \) can be calculated. We found the difficulty that the frequencies collected in the columns of Kellermann’s tables with his figures. This is particularly the case for the three branches \( \omega \left( \frac{Q}{2} \right), \omega \left( \frac{Q}{3} \right) \) and \( \omega \left( \frac{Q}{4} \right) \). But it does not matter greatly as these branches do not differ much.

We have taken means between the 3 and 4 branches and between the 5 and 6 branches corresponding to the results for the central point.

The density for \( 2\omega \left( \frac{Q}{j} \right) \) is taken from Kellermann’s paper ‘On the specific heat of sodium chloride crystal’, where he gives drawings for the density of \( \omega \left( \frac{Q}{j} \right) \) (Kellermann 1941). Following his methods for the other cases the \( \omega \)-scale is divided into equal sections \( \Delta \omega = 0.6 \times 10^{13} \) sec.\(^{-1} \) and the number of frequencies \( \omega \left( \frac{Q}{j} \right) \pm \omega \left( \frac{Q}{j'} \right) \) counted in each interval. By changing the initial point by \( 0.2 \times 10^{13} \) sec.\(^{-1} \) three step curves are obtained for each \( \omega \left( \frac{Q}{jj'} \right) \), which are finally replaced by one smooth curve. The results for the pairs of branches are represented in figure 1.†

One sees already that apart from one group of maxima near zero frequency which will be covered by the width of the exciting mercury line there appear five main groups of maxima. Their mean positions are given in the first row of table 3 and are compared with the peaks observed by Krishnan. The table shows that our theory gives without any arbitrary assumptions the main features of the observed spectrum. A number of small side maxima are to be expected, just as they are found in the photograph, but it would be deceptive to try to include all these in the resultant intensity curve and to compare them with observations, since there is no evidence

† We are indebted to Miss Joan Smith for the calculations of the density distributions of \( \omega \left( \frac{Q}{j} \right) \pm \omega \left( \frac{Q}{j'} \right) \).
that the smaller peaks in the photograph are not chance fluctuations. Therefore we have used the methods described before, namely, the simplified formula (6·5) containing only twelve combinations of branches.

![Graph of \( \varepsilon'_t(\omega) \), density of frequency \( \omega \left( \frac{Q}{j} \right) \pm \omega \left( \frac{Q}{j'} \right) \).](image)

**Figure 1.** Graphs of \( \varepsilon'_t(\omega) \), density of frequency \( \omega \left( \frac{Q}{j} \right) \pm \omega \left( \frac{Q}{j'} \right) \).

| 1. \(2\omega(1)\). | 7. \(\omega(1) + \omega(5), \omega(1) + \omega(6)\). | 13. \(\omega(1) - \omega(5), \omega(1) - \omega(6)\). |
| 2. \(2\omega(2)\). | 8. \(\omega(2) + \omega(3), \omega(2) + \omega(4)\). | 14. \(\omega(2) - \omega(3), \omega(2) - \omega(4)\). |
| 3. \(2\omega(3), 2\omega(4), \omega(3) + \omega(4)\). | 9. \(\omega(2) + \omega(5), \omega(2) + \omega(6)\). | 15. \(\omega(2) - \omega(5), \omega(2) - \omega(6)\). |
| 4. \(2\omega(5), 2\omega(6), \omega(5) + \omega(6)\). | 10. \(\omega(3) + \omega(5), \omega(3) + \omega(6)\). | 16. \(\omega(3) - \omega(4)\). |
| 5. \(\omega(1) + \omega(2)\). | \(\omega(4) + \omega(5), \omega(4) + \omega(6)\). | \(\omega(3) - \omega(5), \omega(3) - \omega(6)\). |
| 6. \(\omega(1) + \omega(3), \omega(1) + \omega(4)\). | 11. \(\omega(1) - \omega(2)\). | \(\omega(4) - \omega(5), \omega(4) - \omega(6)\). |
| 12. \(\omega(1) - \omega(3), \omega(1) - \omega(4)\). | \(\omega(5) - \omega(6)\). |

**Table 3**

<table>
<thead>
<tr>
<th>(\Delta \nu) in cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>density maxima from figure 1</td>
</tr>
<tr>
<td>observed peaks (Krishnan)</td>
</tr>
</tbody>
</table>

Table 4 contains the numerical values of \( \mathcal{C}_j \) and \( e^{-\beta_j} \) for \( Q = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \), \( T = 273^\circ \text{K} \). Using products and squares of \( \mathcal{C}_j \) and the corresponding \( e^{-\beta_j} \) according to formula (6·15) we have redrawn the branches after multiplication by the proper factors,
obtaining a figure which differs only a little from figure 1. Finally, we have tried to fit the maxima to the observed intensities by adapting the $A(jj')$ of (6.14) which depend on the three constants $F$, $G$ and $H$. We found that the simplest relations between $F$, $G$ and $H$ leading to fairly good relative intensities were

$$F + G = 0, \quad H = 0,$$

(7.1)


(7.2)

Considering the number of omissions and simplifications which we have already made it does not seem worth while to improve the results by changing the constants $A(jj')$. It should be possible to determine the coupling constants from first principles by applying quantum mechanics to the interaction between the electronic clouds of neighbouring atoms. We should like to draw attention to the fact that one of the constants $F$ or $G$ appears to be negative (probably $G$).

Figure 2. Fine line is sketch of Krishnan’s microphotometric record of Raman spectrum of rock-salt (Krishnan 1945a). Broken lines represent theoretical contributions to intensity of pairs of branches of frequency. Thick line represents theoretical intensity obtained from superposition of these.

Figure 2 shows the final result. It contains the contributions of the single branches, their superposition and the experimental curve taken from Krishnan’s microphotograph (Krishnan 1945a). The general features of the observations are well

<table>
<thead>
<tr>
<th>$\frac{2G_j}{k} \times 10^{13}$</th>
<th>$\omega(1)$</th>
<th>$\omega(2)$</th>
<th>$\omega(3) = \omega(4)$</th>
<th>$\omega(5) = \omega(6)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.309</td>
<td>0.429</td>
<td>0.855</td>
<td>1.245</td>
</tr>
<tr>
<td>$e^{-\beta_j}$</td>
<td>0.284</td>
<td>0.361</td>
<td>0.512</td>
<td>0.584</td>
</tr>
</tbody>
</table>
represented. If one takes into account that many of the curves are actually double
or triple and that some have been entirely omitted, one would expect that a more
perfect approximation would give an even better agreement.†

Our results show conclusively that the second-order Raman effect cannot be used
to disprove lattice dynamics. The observations not only do not confirm any of the
predictions of Raman’s theory but they represent direct evidence for the existence
and quantitative properties of the continuous spectrum as predicted by correct
mechanical treatment of lattice vibrations.

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† The figure published in our preliminary publication in Nature (1945; see also Krishnan
1946 and Born 1946) differs a little from figure 2 of the text because of a numerical mistake;
we have given one of the branches, $\omega(5)$, double its weight.