

ON THE TRANSFORMATION OF LIGHT INTO  
HEAT IN SOLIDS. II

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## ABSTRACT

The results arrived at in a preceding paper are generalized for diatomic crystals (§§1, 2, 3). A direct determination of the probability of light absorption in a linear lattice leads to the establishment of a selection rule amounting to the law of the conservation of momentum for the light quanta and the "excitation quanta." This rule enables one to explain the linear structure of the spectra of solid bodies at low temperatures (§4). The preceding results are generalized and applied to a new description of the process of light scattering in crystals (§5) and the theory improved by introducing the width of the excitation lines and allowing for the damping of the exciting light waves.

## 1. GENERAL CONSIDERATIONS FOR A DIATOMIC CRYSTAL

**I**N A previous paper under the same title<sup>1</sup> I have limited myself to the consideration of monatomic bodies. The first object of the present note is to generalize the above results for the case of a diatomic (binary) crystal; the further generalization for a more complicated body will be quite obvious and will, therefore, not require special consideration. The main difference between a diatomic (or polyatomic) crystal and a simple one consists in the fact that the heat motion is realized here not only by elastical vibrations, for which the relative positions of the atoms within one molecule are approximately constant, the molecule oscillating as a whole, but also by "molecular vibrations" which can be visualized as the (distorted) vibrations of the atoms constituting the separate molecules, the center of gravity of the latter remaining approximately at rest. Whereas the elastical vibrations have a practically continuous spectrum, extending from  $\nu=0$  up to a certain maximum frequency  $\nu_{\max}$ , the molecular vibrations are usually characterized by one particular frequency  $\nu_c$ , described as the "characteristic ultrared frequency" of the crystal and detected by the absorption and reflection of ultrared light or the Raman scattering of the ordinary light.

As a matter of fact there is no sharp distinction between the vibrations of both types. This is clearly seen if one considers a simple crystal as a limiting case of a diatomic crystal with actually identical atoms of "different sort." Owing to the mutual action of the molecules the vibration frequency  $\nu_0$ , characteristic of an isolated molecule, is split up into a series of  $n$  (or  $3n$ ,  $n$  being the total number of molecules in the crystal) frequencies  $\nu_{c1}, \nu_{c2}, \dots, \nu_{cn}$  which, however, usually lie very close to each other and are, therefore, considered as a single characteristic frequency  $\nu_c$  shifted more or less with respect to  $\nu_0$ . It must, however, be born in mind that the mutual action of the molecules

<sup>1</sup> Frenkel, Phys. Rev. **37**, 17 (1931).

in a crystal produces not simply a shift of their characteristic frequency but causes it to split up into a number ( $3n$ ) of components, corresponding one by one to the various frequencies constituting the elastical spectrum. In fact the corresponding vibrations must have in both cases exactly the same wavelength.

The general theory of the oscillations of a compound crystal lattice has been developed in great detail by M. Born.<sup>2</sup> In this theory Born treated the electrons and nuclei as capable of vibrating about certain equilibrium positions in accordance with the pre-quantum views. We shall have to reserve Born's treatment for the atoms (or ions in a case of an ionic crystal) as *wholes*, the motion of electrons within a single atom being described by specifying the quantum state, normal or excited, of the atom, as has been done in the preceding paper (I). The localization of the excitation state in a particular atom, just as in the case of a simple crystal, does not correspond to a stationary state of the crystal as a whole. Such stationary states are obtained by "diluting" the excitation state over all the atoms *of the same kind* in the form of excitation waves. To a first approximation these excitation waves are not influenced by the presence of atoms of other kinds (which produce a perturbation of the second order only). We thus get exactly the same picture of the excited states or sub-states in the case of a diatomic crystal as that which has been developed before for a simple one.

In the present case, just as in the former one, the excitation of the crystal must entail a slight alteration in its structure, size and vibration frequencies, which will provide an indirect coupling between the different heat oscillators representing these frequencies. To get the looked for generalization of our former theory we need but add to the  $3n$  harmonic heat oscillators representing the elastic spectrum, an equal number of oscillators representing the molecular vibrations. With the same approximation which is implied in assigning to all the latter oscillators the same characteristic frequency  $\nu_c$  we can determine their contribution to the probability of a "deactivation" process by means of the Eqs. (32) and (32a) of I. The probability of a radiationless transition of a diatomic crystal from some excited state or more exactly "sub-state" (2) to the normal state, with the transfer of the excitation energy to  $p$  molecular oscillators is thus proportional to the  $p$ th power of the quantity

$$\mu = \frac{\pi^2 m}{2h} \nu_c (\Delta L)^2 \frac{N}{n} \quad (1)$$

where  $\Delta L = n \cdot \Delta \delta$  is the measure of the change of the distance between the atoms caused by the excitation of the crystal. This quantity must in general have different values for the molecular oscillators on the one hand and the oscillators representing the elastic vibrations on the other. Further, in the former case  $m$  is approximately equal to the sum of the masses of the two atoms of different kind ( $m_a + m_b$ ), whereas in the latter it is given (with the same approximation) by the equation  $1/m = (1/m_a) + (1/m_b)$ .

<sup>2</sup> Born, "Dynamik der Kristallgitter," Leipzig, 1915. *Atomtheorie des festen Zustandes*, Leipzig, 1925.

## 2. QUANTITATIVE THEORY OF A UNIDIMENSIONAL MODEL

For the convenience of the reader we shall briefly sum up here the theory of the vibrations of diatomic crystals, replacing the latter for the sake of simplicity by a one-dimensional model which we shall call a "bar" and which consists of atoms  $a$  and  $b$  in alternating order. The consecutive atoms of different kind may be combined in pairs representing the "molecules." The distance from an atom  $a$  to the next  $b$  on the right of it  $\delta_{ab}$  may be in general different from the distance  $\delta_{ba}$  from  $b$  to the next  $a$  atom in the same direction (Fig. 1). The sum  $\delta_{ab} + \delta_{ba} = \delta$  will represent the lattice constant; the smaller of the two distances  $\delta_{ab}$  and  $\delta_{ba}$  if they are different can be considered as corresponding to that pair of atoms which actually forms a molecule. Denoting

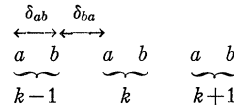


Fig. 1.

the displacements of the atoms forming the  $k$ th molecule from their equilibrium positions with  $u_k$  and  $v_k$  respectively (we shall consider longitudinal displacements only) we can represent the potential energy of the whole system by the expression

$$U' = U - U_0 = \frac{1}{2} \sum_{kl} a_{kl} u_k u_l + \sum_{kl} c_{kl} u_k v_l + \frac{1}{2} \sum_{kl} b_{kl} v_k v_l \quad (2)$$

and write the equations of motion in the form

$$\begin{aligned} -m_a \frac{d^2 u_k}{dt^2} &= \sum_l a_{kl} u_l + \sum_l b_{kl} v_l \\ -m_b \frac{d^2 v_k}{dt^2} &= \sum_l c_{lk} u_l + \sum_l c_{kl} v_l \end{aligned}$$

In case of an unlimited bar ( $k, l$  varying from  $-\infty$  to  $+\infty$ ) these equations admit the solution

$$u_k = A e^{i(p k - \omega t)} \quad v_k = B e^{i(p k - \omega t)} \quad (3)$$

representing waves of frequency  $\nu = \omega/2\pi$  and length  $\lambda = 2\pi\delta/p$  travelling in a definite direction with the velocity  $w = \omega\delta/p$ . Substituting these expressions in the preceding equations and taking into account the fact that the coefficients  $a_{nl}$ ,  $b_{nl}$  and  $c_{nl}$  depend only upon the difference  $l-n$  of the two indices, we get the following two equations for the (complex) amplitudes  $A$  and  $B$ :

$$\left. \begin{aligned} A a_p + B c_p &= A m_a \omega^2 \\ A c_p^* + B b_p &= B m_b \omega^2 \end{aligned} \right\} \quad (4)$$

where

$$\begin{aligned} a_p &= \sum_l a_{0l} e^{ipl}, \quad l_p = \sum_l b_{0l} e^{ipl}, \\ c_p &= \sum_l c_{0l} e^{ipl}, \quad c_p^* = \sum_l c_{10} e^{ipl} = \sum_l c_{0l} e^{-ipl}. \end{aligned} \quad (5)$$

Equating the determinant of (4) to zero, we obtain the following equation for the frequency

$$(a_p - m_a \omega^2)(b_p - m_b \omega^2) = c_p c_p^*$$

whence

$$\omega^2 = \frac{1}{2} \left( \frac{a_p}{m_a} + \frac{b_p}{m_b} \right) \pm \left[ \frac{1}{4} \left( \frac{a_p}{m_a} - \frac{b_p}{m_b} \right)^2 + \frac{c_p c_p^*}{m_a m_b} \right]^{1/2}. \quad (6)$$

It can be easily shown that the negative sign corresponds to the elastical vibrations and the positive to molecular vibrations. The corresponding ratios of the amplitudes  $A$  and  $B$  are:

$$B^\pm : A^\pm = \frac{1}{2} \left( \frac{a_p}{m_a} - \frac{b_p}{m_b} \right) \mp \left[ \frac{1}{4} \left( \frac{a_p}{m_a} - \frac{b_p}{m_b} \right)^2 + \frac{c_p c_p^*}{m_a m_b} \right]^{1/2} : - \frac{c_p}{m_a}. \quad (6a)$$

If the difference  $(a_p/m_a) - (b_p/m_b)$  is very small in regard to  $|c_p| (m_a m_b)^{1/2}$  this equation reduces to

$$B^\pm : A^\pm \cong \pm \left( \frac{m_b}{m_a} \right)^{1/2} \frac{|c_p|}{c_p} = \mp \left( \frac{m_b}{m_a} \right)^{1/2},$$

if one takes into account that the coefficient  $c$  must in this case be real and negative. This result corresponds to the usual approximation implying that in the case of molecular oscillations the atoms belonging to the same molecule are vibrating with opposite phases. The frequency of these vibrations is approximately given by

$$\omega^2 = \frac{1}{2} \left( \frac{a_p}{m_a} + \frac{b_p}{m_b} \right) + \frac{|c_p|}{(m_a m_b)^{1/2}}$$

and is considered to be independent of the "wave number"  $p$  (or  $p\delta/2\pi$ ), which of course is a quite unjustified assumption.

In the case of an unlimited bar the number  $p$  remains arbitrary. If the bar consists of  $n$  molecules, then  $p$  can have only the following series of values  $0, 2\pi/n, (2\pi/n) \cdot 2, \dots, (2\pi/n) \cdot (n-1)$ . Of course, running waves of opposite directions and of the same length (corresponding to  $p_1 + p_2 = 2\pi$ ) have to be combined in this case with the same (or rather conjugate complex) amplitude into standing waves.

The normal co-ordinates  $\xi$  are connected with the displacements  $u_k, v_k$  by means of the equations

$$\left. \begin{aligned} u_k &= \sum_p (\xi_p^+ A_p^+ + \xi_p^- A_p^-) e^{ipk} \\ v_k &= \sum_p (\xi_p^+ B_p^+ + \xi_p^- B_p^-) e^{ipk} \end{aligned} \right\} \quad (7)$$

where  $A_p^\pm, B_p^\pm$  denote the normalized solutions of the Eqs. (4). Solving (7) with respect to the  $\xi$  we get

$$\xi_p^\pm = \sum_k (u_k A_p^{\pm*} + v_k B_p^{\pm*}) e^{-ipk}. \quad (7a)$$

The co-ordinates  $\xi_p^+$  refer to the "molecular" and  $\xi_p^-$  to the "elastical" vibrations.<sup>3</sup>

The expression (2) represents the change of the potential energy of the bar due to the displacement of the atoms. The value of this energy in the equilibrium state  $U_0$  as well as the equilibrium distances  $\delta_{ab}$  and  $\delta_{ba}$  are determined from the conditions

$$\frac{\partial U_0}{\partial \delta_{ab}} = 0 \quad \frac{\partial U_0}{\partial \delta_{ba}} = 0.$$

Now the energy  $U_0$  is slightly different for an excited and a non-excited bar; the same must therefore be true with respect to the distances  $\delta_{ab}$  and  $\delta_{ba}$ . The corresponding changes in the normal co-ordinates can be determined in the same way as in the case of a monatomic crystal, namely, putting  $u_k = k \cdot \Delta \delta$  and  $v_k = k \cdot \Delta \delta + \Delta \delta_{ab}$  in (7a). We shall thus get values<sup>1</sup> of the same order of magnitude both for  $\Delta \xi^+$  and  $\Delta \xi^-$ . In view, however, of the greater frequency in the "molecular" vibrations, their role in the deactivation transitions may be expected to be more important than that of the elastic vibrations according to (S). The increase of frequency is partially reduced, at least for comparatively low temperatures, by the decrease of the average quantum number  $N$  (it must be born in mind that the latter refers not to the initial but to the final state, so that in the initial state  $N$  can be equal to 0; the corresponding vibrations appearing only after the transition).

We shall illustrate the above results by considering the special case  $\delta_{ab} = \delta_{ba} = \frac{1}{2} \delta$  (model of a symmetrical crystal of the NaCl type). We shall further neglect the forces between all but the next atoms (which are assumed to be different) and write accordingly the potential energy  $U'$  in the form

$$U' = \sum_k \frac{1}{2} f [(u_k - v_k)^2 + (u_k - v_{k-1})^2 + (u_{k+1} - v_k)^2]$$

which gives through comparison with (2)

$$a_{kk} = b_{kk} = 2f, \quad c_{kk} = c_{k+1,k} = -f$$

all the other coefficients  $a, b, c$  vanishing.

<sup>3</sup> If we wish to deal with standing waves instead of running ones, the factor  $e^{\pm ipk}$  in the above formula has to be replaced by  $\cos pk$ .

We thus get, according to (5)

$$a_p = b_p = 2f, \quad c_p = -f(1 + e^{ip}), \quad c_p c_p^* = 2f^2(1 + \cos p) = 2f^2 \cos^2 \frac{p}{2}$$

whence with the abbreviations  $1/\mu = (1/m_a) + (1/m_b)$  and  $m = m_a + m_b$ :

$$\omega^2 = \frac{f}{\mu} \left( 1 \pm \left[ 1 - \frac{4\mu}{m} \sin^2 \frac{p}{2} \right]^{1/2} \right).$$

For small values of  $p$ , that is for large wave-lengths  $\lambda = 2\pi\delta/p$ , this reduces to

$$\omega_+ \cong \left( \frac{2f}{\mu} \right)^{1/2}, \quad \omega_- \cong \left( \frac{2f}{m} \right)^{1/2} \frac{p}{2}$$

the latter expression corresponding to a velocity of propagation

$$w = \frac{\omega_- \lambda}{2\pi} = \delta \left( \frac{f}{2m} \right)^{1/2}$$

independent of  $\lambda$ . As the wave-length decreases,  $\omega_-$  increases and  $\omega_+$  decreases. For the shortest wave-length corresponding to  $p = \pi$  we have

$$\omega_{+\text{min}}^2 = \frac{f}{\mu} \left( 1 + \left( 1 - \frac{4\mu}{m} \right)^{1/2} \right), \quad \omega_{-\text{max}}^2 = \frac{f}{\mu} \left( 1 - \left( 1 - \frac{4\mu}{m} \right)^{1/2} \right).$$

In the particular case  $m_a = m_b$  when the atoms  $a$  and  $b$  can be considered as identical, these two limits coincide (since  $4\mu = m$ ) and the two spectra, the molecular and the elastical, coalesce into one single elastical spectrum determined by  $\omega^2 = f/\mu(1 \pm \cos p/2)$  which is equivalent to the usual formula

$$\omega^2 = \frac{2f}{m} (1 - \cos p') = \frac{4f}{m} \sin^2 \frac{p'}{2}$$

with  $p' = (2\pi/2n)s$ ,  $s = 0, 1, 2, \dots, 2n-1$ .

### 3. MOLECULAR VIBRATIONS AS EXCITATION WAVES

The opposite limiting case when the two atoms have a very much different mass or when the distance  $\delta_{ab}$  is different from  $\delta_{ba}$  so that the molecular structure is more or less preserved within the crystal (represented by our "bar"), the molecular oscillations can be treated by a method entirely different from the preceding one (which must be preserved for elastic oscillations) and quite similar to that which has been used to describe the motion of the electrons within the individual atoms. We can namely describe the state of an individual molecule by specifying its vibrational quantum number  $N$ , referring to this state as "normal" if  $N=0$  and "excited" if  $N>0$ . The stationary states of the crystal will be then described by "excitation waves" quite analogous to those which were introduced for the description of the electronic state. In fact we have but to replace the atoms and electrons of our previous theory by molecules and atoms respectively, to get these new "mole-

cular" excitation waves. The latter will be represented by functions

$$\chi_p = \sum_k \frac{1}{n^{1/2}} e^{ipk} \phi_k \quad (8)$$

$\phi_k$  being the product of the oscillator wave functions,  $\psi_N$  for the separate molecules, supposed to be all in the normal state  $N=0$  with the exception of the  $k$ th molecule which may be in a given ( $N$ th) excited state. The excitation wave defined by (8) corresponds to the "molecular oscillation wave" of the classical theory given above and associated with the normal co-ordinate  $\xi_p^+$  defined by (7a). The quantum number  $N$  of the excited molecule defines the amplitude of the oscillations and must coincide with the quantum number of the quantized oscillator describing them. The method of the excitation waves is nothing but a first approximation given by the perturbation theory to the exact quantum treatment which in our case consists in the preliminary introduction of the normal co-ordinates and their subsequent quantization and which has been used in the preceding section. It may be remarked that this method cannot be applied to the "elastic oscillations" because they are determined *solely by interaction forces*, which can be dealt with as perturbing forces then only if there are other more powerful forces associated with the separate particles (i.e., forces holding the electrons within the atoms, or the atoms within the molecules).

The theory of the excitation waves as developed in I was restricted to the simplest special case of the excitation if a single atom. Its application to molecular vibrations implies therefore that the excitation is restricted to one molecule only. So long, however, as the molecular vibrations are considered as strictly harmonic this limitation has no practical significance, a complex excitation state corresponding to  $n_1$  molecules having  $N_1$  quanta,  $n_2$  having  $N_2$  quanta and so on being practically equivalent to a simple excitation state with one molecule having  $n_1 N_1 + n_2 N_2 + \dots$  quanta (this multiple excitation is of course diluted over all the molecules in the sense that it is not associated with a particular molecule, but is, so to say, travelling from one molecule to another).

Applying to molecular vibrations the method of the simple excitation waves, one can treat the radiationless transitions of the energy of a crystal from molecular vibrations to elastic ones or *vice versa* (that is the exchange of energy between the normal co-ordinates  $\xi^+$  on the one hand and  $\xi^-$  on the other) in exactly the same way, as this has been done above for radiationless electronic transitions. In the present case the direct coupling between the different elastic oscillations must play a much more important role with respect to the indirect coupling (provided by the change in structure which is produced by molecular vibrations) than in the case of electronic transitions, since the energy quantum of the molecular vibrations is not a 100 times but at most only 10 times as large as that of the elastic vibrations of maximum frequency.

The transitions of energy between different elastic oscillations (that is between different  $\xi^-$ ) must of course entirely depend on direct coupling only.

Such transitions have been studied in detail by R. Peierls<sup>4</sup> in connection with the theory of heat conduction in crystals.

The treatment of the molecular oscillations by the method of excitation waves entails some formal modifications of the theory of the radiationless electronic transitions so far as the electronic excitation energy is transformed into the molecular excitation energy.

We shall not stop, however, on this question here, and shall now proceed to the investigation of radiation transitions, i.e. transitions accompanied by the absorption or emission of light, with a view of introducing an important amendment to the results of the last section of I, dealing with such transitions.

4. SELECTION RULE FOR TRANSITIONS DUE TO ABSORPTION OF LIGHT; ANALYSIS OF THE SPECTRUM OF CRYSTALS AT VERY LOW TEMPERATURES

We shall again confine ourselves, for the beginning, to the case of a monoatomic crystal, represented by a linear model and shall determine the probability of the absorption of light propagated in the direction of our "bar."

We shall first suppose the light wave to be harmonic (infinitely narrow spectral line) and travelling in the same way as if there were no bar, so that the electric intensity at a point  $x$  along the bar will be represented by

$$E = E^0 \cos 2\pi(\nu t - \alpha x) \tag{9}$$

its value at the  $k$ th atom thus being

$$E_k = E^0 \cos (\omega t - qk) \tag{9a}$$

where  $\omega = 2\pi\nu$  and  $q = 2\pi\alpha\delta = 2\pi\delta/\lambda$ ,  $\lambda = c/\nu$  being the wave-length of the light in vacuo. Denoting the electric moment of the  $l$  th atom in the direction of  $E$  (which is of course perpendicular to  $X$ ) with  $U_l$ , we get the following expression for the perturbation energy:

$$V = -\frac{E^0}{2} \sum_{l=1}^n U_l (e^{i(ql-\omega t)} + e^{-i(ql-\omega t)}). \tag{10}$$

If our bar was initially in the normal electronic state

$$\chi_0 = \chi_0^0 e^{-i2\pi W^0 t/h}$$

( $\chi_0^0$  being a function of the electron co-ordinates alone) the probability that it will be switched to the excited (sub) state  $\chi_p = \chi_p^0 e^{-i2\pi W_p t/h}$  without any alteration of the vibrational states is determined by the matrix element

$$V_{0p} = \int V \chi_0 \chi_p^* d\tau$$

where  $d\tau = d\tau_1 \cdot d\tau_2 \cdot \dots \cdot d\tau_n$  is the volume element of the electronic configuration space ( $d\tau_k$  referring to the  $k$ th atom). According to (10) and (8) (the latter expression holding both for electronic and molecular excitation waves

<sup>4</sup> R. Peierls, Ann. der Physik, 1930.



with a corresponding meaning of the functions  $\phi$  and  $\psi$ , see I), this matrix element assumes the form

$$V_{0p} = -\frac{E^0}{2(n)^{1/2}} \left[ e^{-i(\omega+\omega_{0p})t} \sum_k \sum_l e^{i(p-k+q)l} \int U_l \phi_0^0 \phi_k^{0*} d\tau \right. \\ \left. + e^{i(\omega-\omega_{0p})t} \sum_k \sum_l e^{i(p-k-q)l} \int U_l \phi_0^0 \phi_k^{0*} d\tau \right]$$

where  $\omega_{0p} = 2\pi(W_p - W_0)/h$  and  $\phi_0^0 = \chi_0^0$ . Now the integral  $\int \mu_l \phi_0^0 \phi_k^0 d\tau$  can be easily shown to be different from zero in the case only if  $k=l$  (cf. I. p. 20) in which case it reduces to

$$U^0(\text{I, II}) = \int U_k \psi_I^0(x) \psi_{II}^{0*}(k) d\tau_k$$

i.e., to the amplitude of the matrix element of the electrical moment of any one of the atoms for the normal and the excited state of this atom.

The preceding expression for  $V_{0p}$  is thus reduced to

$$V_{0p} = -\frac{E^0 U^0(\text{I, II})}{2(n)^{1/2}} \left[ e^{-i(\omega+\omega_{0p})t} \sum_k e^{i(p+q)k} \right. \\ \left. + e^{i(\omega-\omega_{0p})t} \sum_k e^{i(p-q)k} \right] \quad (11)$$

We need here only to consider the second term in the bracket for the first term will not contribute appreciably to the transition probability in the neighborhood of the "resonance condition"  $\omega = \omega_{0p}$  or  $h\nu = W_p - W_0$ . In addition to this condition which, from the corpuscular viewpoint is interpreted as the equation of the conservation of energy and which would hold just as well in the case of a single atom, we have to consider in our case a second condition of the same "resonance" type, namely  $p=q$ , which corresponds to sharp maximum of the sum  $\sum_k e^{i(p-q)k} = n$  (this maximum is sharper the larger the number of atoms). This second "resonance" condition can be interpreted as the equation of the conservation of *momentum* if we assume that an excitation wave can be associated with an "excitation quantum" similar to a light quantum and having a momentum  $h/\lambda$  where  $\lambda$  is the corresponding wave-length. It may be remarked that the energy of this excitation quantum whose motion represents the travelling of the excitation through the crystal—is not related to the frequency of the excitation wave but is equal to the difference between the energy of the excited and normal state.

The absorption of light by a crystal can be thus visualised from the corpuscular point of view as the transformation of the incident light quantum into an excitation quantum having the same energy and *momentum*.

From the wave point of view the latter condition amounts simply to the equality between the wave-length of the exciting light ( $2\pi\delta/q$ ) and that of the resulting excitation wave ( $2\pi\delta/p$ ).

This condition can be regarded as a kind of "selection rule" reducing the  $n$  spectral lines corresponding to transitions between the normal state and the  $n$  excited substates, to a single line, for which both the frequency (energy) condition  $\nu = W_p - W_0/h$  and the wave-length (momentum) condition  $\lambda_{\text{light}} = \lambda_{\text{exc}}$  are simultaneously satisfied.

It must be emphasized that the conditions  $\nu = (W_p - W_0)/h$  and  $\lambda_{\text{light}} = \lambda_{\text{exc}}$  are *not equivalent* to each other and actually provide two equations for the unambiguous determination of  $\nu$ . We have in fact, according to Eq. (15) of part I (for the unidimensional case)

$$W_p = V_0 + 2 V_1 \cos p/2 \quad (12)$$

whence with the abbreviations  $(V_0 - W_0)/h = \alpha$  and  $2V_1/h = \beta$

$$\nu = \alpha + \beta \cos p/2$$

On the other hand we have  $\lambda_{\text{exc.}} = 2\pi\delta/p$  or, since  $\lambda_{\text{exc.}} = \lambda_{\text{light}} = c/\nu$ ,  $p = (2\pi\delta/c)\nu$  so that finally

$$\nu = \alpha + \beta \cos (\pi\delta/c)\nu \quad (12a)$$

This equation has in general only one solution which can be found to a first approximation by substituting in the right side of (12a) the "zero approximation"  $\nu = \alpha$  (so long as  $\beta$  is small compared with  $\alpha$ ) which gives

$$\nu \cong \alpha + \beta \cos \frac{2\pi\delta\alpha}{c} \quad (12b)$$

Thus, contrary to the view expressed at the end of I, the absorption spectrum of a crystal so far as transitions from the normal state are concerned which are not accompanied by a change of the vibrational state, *should not consist of continuous bands corresponding to the excitation multiplets, but of single lines corresponding one to one to the absorption lines of an isolated atom.*

This result provides an explanation of the remarkable phenomenon referred to in I, that the absorption spectra of solid bodies which at ordinary temperatures consist of continuous bands, at very low (liquid hydrogen or liquid helium) temperatures become more or less *linear*, as those of gases.

In fact the band structure of these spectra at ordinary temperatures must be attributed entirely to vibrational transitions which accompany the electronic ones, and which we did not take into account in the preceding considerations. The probability that a number of "heat oscillators," elastic or molecular, will participate in the electronic transition associated with light absorption, is determined in exactly the same way as in the case of radiationless transitions; provided, namely, that each oscillator  $s$  jumps over one step only, it is represented in the expression of the resulting transition probability by the square of the factor (1), or rather of the factor

$$n_{\mu} = \frac{\pi^2 m}{2h^2} (\Delta L) N_s \nu_s \quad (1')$$

the number  $n$  in the denominator of (1) being cancelled by the factor expressing the number of possible ways of choosing this oscillator (the total number  $p$  of the latter participating in the transition being represented by a factor  $p!$  in the denominator of the resulting probability). Now since  $hN_s\nu_s$  denotes the vibrational energy of the respective oscillator (without the constant part  $\frac{1}{2}h\nu_s$ ) which rapidly decreases as the temperature approaches the absolute zero, it is clear that the participation of the heat oscillators in the electronic transitions must become less and less active, which will result in the gradual splitting up of the absorption bands into single lines.<sup>5</sup>

It must be remembered that  $N_s$  in the preceding expression denotes the vibrational quantum number of the initial state if it *decreases* during the transition ( $N_s \rightarrow N_s - 1$ ); in the contrary case which is in general the more important one,  $N_s$  means the vibrational quantum number in the final state; for the absolute zero of temperature upward jumps of  $N_s$  are only possible with the final value  $N_s = 1$  (since the initial is zero). The same formula (1') shows that in this case, i.e., with all the  $N_s$  equal to 1, the probability that an oscillator will participate in the transition is proportional to the square of its frequency. Therefore at very low temperatures practically oscillators of the highest frequency only i.e. the molecular oscillators, and to some extent the elastic oscillators with the highest frequency  $\nu_{\text{max}}$  ("characteristic frequency" of Debye), will participate in the transitions.<sup>6</sup> In the case of a simple (monoatomic) crystal only the latter come into consideration. We are lead thus to expect that the absorption spectrum of a monoatomic (non-metallic) crystal at or near the zero point of temperature must consist of *groups* of lines, corresponding to the absorption lines of an isolated atom, each group consisting of a series of equidistant lines with the constant spacing  $\Delta\nu = h\nu_{\text{max}}$ . The lowest frequency line must have the largest intensity for it must correspond to the purely electronic transition, the next one, with a shorter wave-length and smaller intensity to a transition associated with the upward jump of one oscillator, the next with a still shorter wave-length and still smaller intensity, to a transition associated with the upward jump of two oscillators and so on. These lines must have a sharp edge on the high-frequency side and a rather diffuse one on the other side (since elastic oscillators of lower frequency will also, to some extent, participate in the transitions).

So far as the "selection principle" derived above for a monoatomic crystal (i.e. the condition  $\lambda_{\text{light}} = \lambda_{\text{exc.}}$ ) remains valid for a diatomic one, which can easily be shown to be the case, the preceding analysis of the zero-point spectrum can be immediately extended on diatomic crystals. In this case each

<sup>5</sup> At the same time will decrease the natural width of these lines which is proportional to the probability of a radiationless transition from the excited state into the normal one.

<sup>6</sup> The predominance of these oscillators is insured not only by their higher frequency but also in a three dimensional crystal, by their larger number, the number of oscillators with a frequency between  $\nu$  and  $\nu + d\nu$  being proportional to  $\nu^2 d\nu$ .

group of lines corresponding to a particular absorption line of one of the atoms (if they are different<sup>7</sup>) must be subdivided into two groups, the spacing in the one being  $h\nu_{\text{max}}$  and in the other  $h\nu_c$ ,  $\nu_{\text{max}}$  being as before the maximum frequency of the elastic spectrum, and  $\nu_c$  the molecular vibration frequency. The lines of the second group can be expected to have larger intensities than those of the first. In both cases increasing frequency must correspond to decreasing intensity.

As the temperature increases the satellites, due to the participation in the transitions of the elastic oscillators, must become more and more diffuse on the short frequency side, owing to the rapid increase of the energy  $N_s h\nu_0$  and consequently the "activity" (in the sense of their participations in the transitions) of the lower frequency oscillators until each group of lines will be transformed into a diffuse continuous band. Thus on our theory the continuous character of the absorption bands in the spectra of solid bodies at ordinary temperatures is to be ascribed to the equi-partition of energy between the elastic oscillators of different frequencies, resulting in an equal participation of all these oscillators in the transitions associated with the absorption of light.<sup>8</sup>

#### 5. GENERALIZATION OF THE THEORY AND APPLICATION TO THE SCATTERING OF LIGHT

The conclusions of the preceding paragraph have been reached on the basis of a result ("selection principle") whose derivation has been neither general, for we have limited ourselves to a unidimensional model of a monoatomic crystal, that was supposed to be initially in the normal state, and did not take into account the vibrational motion, nor rigorous, for we have assumed that the incident light wave were travelling through the crystal, as if the latter was absent, and did not allow for the finite spectral width of this light.

We must now remove these defects and thereafter revise the above conclusions in the light of the improved theory.

(a) We shall examine first of all the generalization from the unidimensional to the three-dimensional crystal lattice. This generalization amounts to the replacement of the numbers  $k$ , specifying the position of a given atom in the lattice by triplets of numbers  $k_1, k_2, k_3$  which can be considered as components of a vector  $\mathbf{k}$  and a similar substitution of vectors  $\mathbf{p}$  and  $\mathbf{q}$  for the scalars  $p$  and  $q$  characterizing the wave-length of the excitation waves and of the light waves. The direction of these vectors defines the direction in which the respective waves are propagated; their magnitude is connected with the wave-length in the same way as before ( $\lambda_{\text{light}} = 2\pi\delta/q$ ,  $\lambda_{\text{exc.}} = 2\pi\delta/p$ ). The components of the vector  $\mathbf{p}$  can of course assume values of the type  $p_i = 2\pi r_i/n_i$  where  $r_i$  are integers and  $n_i$  denote the numbers of atoms along

<sup>7</sup> If they are identical we have to deal with a molecular lattice and compare its spectrum, not with that of one of the atoms, but rather with that of an isolated non-rotating molecule.

<sup>8</sup> Another cause of the broadening of the lines lies in the radiationless transitions from the excited state into the normal one, the probability of the the transitions being a measure of the breadth of the lines. It is, however, difficult to estimate the value of this breadth.

the different edges of the crystal (supposed to be of rectangular shape and to have a cubical lattice with the constant  $\delta$ ).

The formula (11) which serves to determine the transition probability will remain valid for the three-dimensional case if the product of  $p_k$  and  $q_k$  is replaced by the *scalar products* of the corresponding vectors. As a result we shall obtain our "selection principle" in the form  $\mathbf{p} = \mathbf{q}$  expressing the equality not only of the magnitudes of the vectors  $\mathbf{p}$  and  $\mathbf{q}$  but also of their directions, or from the point of view of the quantum interpretation, the transformation of the incident light quantum into an excitation quantum with a momentum of the same magnitude and direction.

(b) The generalization of the preceding result for a diatomic (or many atomic) crystal is quite simple. We have, namely, seen that in case of *different* atoms the excitation waves for the atoms of one kind are to a first approximation completely independent of the presence of the atoms of the other kind. Equation (11) in the "vectorized" form will, therefore, apply to the atoms of each kind separately.

The situation is somewhat different if the atoms supposed to be of different kind differ only with respect to their position, but are actually of the same kind. This corresponds to a molecular lattice, such as the lattice of  $I_2$  (solid iodine) for example. In this case it is convenient to replace the atoms as elements of the crystalline structure by the molecules and deal with the molecular vibrations in the same way as with the electronic ones, i.e. describe them by means of the excitation waves.

(c) This remark brings out the following interesting point. We have just shown that the excitation waves must be associated with "excitation quanta" possessing a momentum in the direction of propagation, and that the "selection principle"  $\mathbf{p} = \mathbf{q}$  can be regarded as the equation of the conservation of momentum in the process of the absorption of a light quantum. Now if molecular vibrations (both in the case of equal or different atoms) are described by excitation waves, it seems possible to combine an electronic transition with a transition of some molecular vibration type in such a way that the equation  $\mathbf{q} = \mathbf{p}$  should be replaced by an equation  $\mathbf{q} = \Sigma \mathbf{p}$  for the different excitation waves involved in the transition, so that the electronic transitions will no longer be restricted by the above selection principle.

This argument is, however, erroneous. Let us remark first of all that if a few different types of excitation waves (corresponding to states with approximately the same energy) would be generated simultaneously forming a combined wave of the type  $\chi = c' \chi_{p'} + c'' \chi_{p''} + \dots$  the momentum equation would run  $\mathbf{q} = |c'|^2 \mathbf{p}' + |c''|^2 \mathbf{p}'' + \dots$ . It can further be easily seen that it should be fulfilled for each of the constituting waves (representing a stationary excited state) separately, so that  $\mathbf{q} = \mathbf{p}' = \mathbf{p}'' = \dots$ . Since  $|c'|^2 + |c''|^2 + \dots = 1$  the preceding equation actually reduces to  $\mathbf{q} = \mathbf{p}$  for any one of the waves.

It must finally be born in mind that such excitation waves can be generated only for which the matrix element of the electric moment / (I, II) of an atom, or a molecule, is different from zero. In case of a diatomic homopolar

crystal of the type of  $I_2$  this condition would obviously not be satisfied for excitation waves of a purely molecular vibration type. In general the proportionality of  $V_{0p}$  to  $U(I, II)$  shows that excitation waves can be generated only which correspond to the optically excitable states of the separate atoms or molecules of which the crystal is built up.

It follows from the preceding considerations that the vibrational motion of the atoms (or molecules) in a crystal, or the transitions from one vibrational state to another, which may accompany the electronic transitions, do not impair the "selection principle" provided by the equation  $q = p$  for these electronic transitions.

This result requires but a very slight amendment in connection with the following circumstances. In consequence of the vibrational (heat) motion the atoms no longer form a regular lattice, which they were assumed to form in the derivation of the above equation. Taking again for the sake of simplicity the case of a linear lattice we can define the displacements of the atoms from their equilibrium positions by adding to their ordinal (integral) numbers  $k$  small fractions  $u_k$ , whose products with  $\delta$  are equal to the respective displacements. Now  $u_k$  can be represented as a superposition of Debye waves in the form

$$u_k = \sum_{p'} a_{p'} e^{i(p'k - \omega' t)}$$

where  $a_{p'}$  are very small amplitudes.

The factors  $e^{\pm i q l}$  in the perturbation function (10) must be replaced accordingly by  $e^{\pm i q(l+u)}$  or, since  $u$  is very small, by  $e^{\pm i q l}(1 \pm i q u)$ . Effecting the same substitution in (11) we must replace  $\omega - \omega_{0p}$  by  $\omega - \omega_{0p} - \omega'$  and the sum  $\sum_k e^{i(p-q)k}$  whose maximum value has to be sought for the determination of our "selection principle" by

$$\sum_k e^{i(p-q)k} - i q \sum_{p'} a_{p'} \sum_k e^{i(p-p'-q)k}. \quad (13)$$

The latter expression has besides the main maximum for  $p = q$  secondary maxima for  $p = q + p'$  which can be interpreted from the quantum corpuscular point of view as the equations for the conservation of momentum of the light quanta, excitation quanta and "heat-quanta" or "sound-quanta" corresponding to the Debye waves. The resonance condition for the frequencies  $\omega = \omega_{0p}$  is in *all cases* replaced by  $\omega = \omega_{0p} + \omega'$  which can be interpreted as the energy equation for the above three types of quanta.<sup>9</sup> This equation is consistent both with the equation  $p = q + p'$  and with the equation  $p = q$  which means simply that in the transition process two standing sound waves of opposite directions, forming a standing wave with no resulting momentum, are generated. Since the main maximum of the expression (13) which is approximately equal to the number of atoms  $n$  is much more important the secondary ones

<sup>9</sup> These results are identical with those obtained by Ig. Tamm in his rather elaborate theory of the scattering of light in crystals. The notion of "sound quanta" is also due to this author.

which have the order of magnitude of  $nqa$ , the vibrational motion of the atom has practically but a very small influence on the position of the groups of absorption lines in the spectrum of the crystal. Nevertheless we must be prepared to find with rising temperature new groups in the form of continuous bands to appear which correspond to the "unusual" selection rules  $p = q + p'$  and whose intensity must increase linearly with the absolute temperature (in the equipartition region).

(d) The last generalization that we have to carry out is the allowance for absorption transitions not from the normal state to an excited one, but from one excited  $\chi_{p'}$  state to another  $\chi_{p''}$  (with a higher energy). It is clear that the preceding results will still be valid for this case if we replace  $\omega_{0p} = 2\pi(W_p - W_0)/h$  by  $2\pi(W_{p''} - W_{p'})/h$  and the vector  $p$  by the vector difference  $p'' - p'$ , so that the two "resonance conditions" for the frequencies and the wave-lengths, i.e., the equations of conservation of energy and momentum, assume the form

$$h\nu = \frac{W_{p''} - W_{p'}}{h}, \quad q = p'' - p' \left( q = \frac{2\pi\delta}{\lambda_{\text{light}}}, \quad p' = \frac{2\pi\delta}{\lambda_{\text{exc}'}}}, \quad p'' = \frac{2\pi\delta}{\lambda_{\text{exc}''}} \right)$$

if the effects of the heat motion and if the corresponding (vibrational) transitions are neglected.

The preceding results must obviously hold not only for the absorption but also for the emission of light (in a definite direction) and can be still further generalized to allow for its scattering (by replacing  $\nu$  and  $q$  by the differences  $\nu' - \nu''$  and  $q' - q''$  for the incident and scattered light). We shall not engage into a detailed investigation of this question and shall satisfy ourselves with the following remarks. *First*, that the present theory of light scattering in crystals so far as the relations between energy (frequency) and momentum (wave number) are concerned is the exact analogon to Schrödinger's theory of the Compton effect, i.e., of the scattering of light by free electrons, the electron waves being replaced in our case by the excitation waves. In fact the above considerations form the basis of a theory of the Raman effect, which, as well known, is the analogon of the Compton effect for bound electrons and atoms bound together into molecules. The analogy between the two effects is most clearly brought out by means of the conception of the excitation waves as the analogon of cathode waves. *Second*, that the Raman shift of the frequency of the incident light  $\nu' - \nu''$  can be calculated either by considering molecular vibrations by the method of excitation waves, or by incorporating them into the heat motion and allowing for the latter according to section (c). *Third*, that the development of the theory sketched above in the quantitative direction, i.e. to enable one to calculate the intensity of the scattered lines, both shifted and unshifted, does not present any difficulty, for this calculation can be easily reduced to the corresponding calculation for an isolated atom or molecule (if the molecular vibrations are described by excitation waves).

6. IMPROVEMENT OF THE THEORY; FINITE WIDTH OF THE EXCITATION LINES, AND INFLUENCE OF THE DAMPING OF THE LIGHT WAVES

We must now turn to the improvement of our theory of light absorption with respect to rigour.

(a) We have assumed the light to be strictly homogeneous, which of course is not the case. This circumstance can, however, easily be taken into account in exactly the same as this is done for a single atom. The result will be that the probability of the transition  $\chi_0 \rightarrow \chi_p$  in the case of a linear crystal lattice considered in §4 will be equal to the probability of the corresponding transition for a single atom (which is proportional to  $|U(I, II)|^2$ ) multiplied with the square of the modulus of the factor

$$S = \frac{1}{n^{1/2}} \sum_{k=1}^n e^{i(p-q)k} \tag{13a}$$

(cf. Eq. (11)). The maximum value of the sum  $\sum e^{i(p-q)k}$  for  $p=q$  being  $n$ , the total probability for the light absorption by the crystal turns out to be equal, for the lines "allowed" by the "selection rule"  $p=q$ , to  $n$  times the corresponding probability for a single atom. This is just what would be expected on the assumption that the atoms of the crystal do not influence the propagation of the light waves.

The result obtained, which obviously holds for a three-dimensional crystal lattice just as well as for a unidimensional one, requires strictly speaking, some modification. In calculating the transition probability under the action of a spectral line of finite width, one has to take into account the variation of  $q = 2\pi\delta/\lambda = \delta\omega/c$  in the factor (12a) with the frequency of the light  $\nu = \omega/2\pi$ . This would amount to replacing the product of  $|S|^2$  with the integral

$$\int_{-\infty}^{+\infty} \left| \frac{e^{i(\omega-\omega_{0p})t} - 1}{\omega - \omega_{0p}} \right|^2 d\omega$$

occurring in the theory of light absorption by a single atom by the integral

$$\int_{-\infty}^{+\infty} \left| \frac{e^{i(\omega-\omega_{0p})t} - 1}{\omega - \omega_{0p}} \right|^2 |S|^2 d\omega$$

It can be easily shown, however, that maximum of  $|S|$  about  $q=p$  is much flatter than the maximum of the function

$$\left| \frac{e^{i(\omega-\omega_{0p})t} - 1}{\omega - \omega_{0p}} \right|^2 = \frac{\sin^2 (\omega - \omega_{0p})t/2}{((\omega - \omega_{0p})/2)^2}$$

about the corresponding point  $\omega = \omega_{0p}$  so that in carrying out of the integration  $|S|^2$  can be replaced by its maximum value ( $n$ ) corresponding to  $\omega = \omega_{0p}$  with a proper choice of  $p$ , of course. The dependence of  $|S|^2$  on  $q-p$  can be easily determined. We have namely for a unidimensional lattice if  $k$  is varied from 0 till  $n-1$



$$S = \frac{1}{n^{1/2}} \frac{e^{i(p-q)n} - 1}{e^{i(p-q)} - 1}$$

whence

$$|S|^2 = \frac{1}{n} \frac{\sin^2 n(p-q)/2}{\sin^2 (p-q)/2}. \quad (13b)$$

The effective width of the maximum of  $|S|^2$  can thus be determined for a definite value of  $q$  and a variable  $p$  by

$$\Delta(p-q) = \Delta p \cong 2\pi/n$$

or, since  $p = 2\pi\delta/\lambda_{\text{exc}}$  ( $\lambda_{\text{exc}}$  = wave-length of the excitation wave)

$$\frac{|\Delta\lambda_{\text{exc}}|}{\lambda_{\text{exc}}} = \frac{\lambda_{\text{exc}}}{n\delta} = \frac{\lambda_{\text{exc}}}{L} = \frac{\lambda_{\text{light}}}{L} \quad (14)$$

where  $L = n\delta$  is the total length of the lattice.

This result can be easily generalized for the case of a three-dimensional lattice,  $L$  denoting in this case one average linear dimension of the latter. The width of the absorption region, i.e., the frequency interval  $\Delta\nu$  for which transitions from the normal state to excited sub-states can take place according to our "unsharp" selection rule is given according to (12) by

$$\Delta\nu = \frac{\beta}{2} \sin \frac{p}{2} \Delta p$$

that is

$$\Delta\nu = \frac{\pi V_1}{hn} \sin \frac{\pi\delta}{\lambda} \quad (14a)$$

where  $\lambda$  can be identified with the wave-length of the light. Since  $\delta/\lambda$  is for ordinary light a very small quantity we can put  $\sin(\pi\delta/\lambda) = \pi\delta/\lambda$  and consequently

$$\Delta\nu = \frac{\pi^2 V_1}{h} \frac{\delta}{L}. \quad (14b)$$

Thus the width of the absorption lines, so far as the vibrational transitions are not taken into account, remains very small at least for crystals of ordinary size. The incompleteness of "resonance" with respect to the wave-lengths, i.e., the departure of  $\lambda_{\text{light}} - \lambda_{\text{exc}}$  from zero, does not therefore contribute appreciably to the width of the lines. At very low temperatures this width must be determined mainly by the probability of the radiationless transitions, whereas at higher temperatures the linear pattern of the spectrum is wiped out by the participation of the low frequency heat (sound) vibrations in the transitions as has been explained above (§4).

(b) It remains for us now to take into account the fact that the propagation of light in a real three-dimensional crystal is substantially affected by the latter, especially in the region of selective absorption, with which we are particularly interested. This influence can be accounted for by replacing the vacuum wave-length of the light  $\lambda_0$  or the corresponding quantity  $q = q_0 = 2\pi\delta/\lambda_0$  by a certain complex quantity  $q = q_1 - iq_2$  determining the effective wave-length  $\lambda_1 (q_1 = 2\pi\delta/\lambda_1)$  and the absorption coefficient  $q_2/\delta$ .

In the case of the unidimensional lattice ("bar") considered above, the intensity factor (13a) assumes under this condition the form

$$S = \frac{1}{n^{1/2}} \frac{e^{i(p-q_1)-q_2} - 1}{e^{i(p-q_1)-q_2} - 1}$$

whence

$$|S|^2 = \frac{1}{n} \frac{1 - 2e^{-q_2 n} \cos(p - q_1)n + e^{-2q_2 n}}{1 - 2e^{-q_2} \cos(p - q_1) + e^{-2q_2}}$$

For large values of  $n$  this reduces to

$$|S|^2 = \frac{1}{n} \frac{1}{1 - 2e^{-q_2} \cos(p - q_1) + e^{-2q_2}} \quad (15)$$

the maximum of this expression for  $p - q_1 \cong 0$

$$|S|^2 = \frac{1}{n(1 - e^{-q_2})^2} \quad (15a)$$

being of course smaller and flatter than in the case of  $q_2 = 0$ . The flatness of this maximum must increase the width of the absorption lines and might in fact lead to their transformation in comparatively broad bands even without the participation of the low frequency vibrations. The width of the maximum of  $|S|^2$  may be roughly put equal to  $q_2$  if  $q_2$  is sufficiently small, which gives for  $\Delta\nu$  the effective width of the absorption line, the expression

$$\Delta\nu \cong \frac{V_1}{h} q_2 \sin \frac{p}{2} = \frac{\pi V_1 q_2 \delta}{h\lambda} \quad (16)$$

The ratio  $q_2/\delta$  represents the value of the absorption coefficient of the light per unit length of path and its product with  $\lambda$ ,  $q_2\lambda/\delta = \mu$  the absorption coefficient per wave-length. Substituting this in the preceding formula we get

$$\Delta\nu = \frac{\pi V_1}{h} \mu \left( \frac{\delta}{\lambda} \right)^2 \quad (16a)$$

This formula shows that unless  $\mu$  is unreasonably large  $\Delta\nu$  remains actually small. It may be remarked that the ratio  $V_1/h$  represents a frequency which is about at least 10 times smaller than the frequency of ordinary light.

The preceding results can be easily generalized for the case of an ordinary three-dimensional crystal.

(c) In conclusion the following point should be noted. Since the resonance conditions for the frequencies and for the wave-lengths are both unsharp, the excitation state of the crystal induced by the absorption of light must be represented not by *one* definite excitation wave, but by a superposition of a number of such waves with approximately equal lengths and frequencies, i.e. by a group of excitation waves. The corresponding group velocity can be considered as the velocity with which the "excitation quantum," i.e., the excitation state supposed to be localized in a definite atom and described as a corpuscle, should travel through the crystal (cf. I, §2).