JANUARY 1, 1931 PHYSICAL REVIEW VOLUME 37

ON THE TRANSFORMATION OF LIGHT INTO HEAT IN SOLIDS. I[1]

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(Received November 25, 1930)

ABSTRACT

Starting from the analogy between a crystal and molecule, it is shown that the electronic excitation, forming the first step in the process of light absorption, is not confined to a particular atom, but is diluted between all of them in the form of "excitation waves," similar to sound waves which are used to describe the heat motion in the same crystal. Owing to the interaction between the atoms the excitation state is split up into substates whose number is equal to the number of atoms n (excitation multiplet). By superposing several excitation waves "excitation packets" can be constructed representing the travelling of the excitation state from one atom to another. To each excitation sub-state there corresponds a definite crystal structure (lattice constant, vibration frequencies) slightly different from that of the normal, and giving rise to slightly different vibrational states. This influence of the excitation on the vibrational states provides an indirect coupling between them, which allows the excitation energy to be shared between a few hundred heat-oscillators with practically no direct coupling nor anharmonicity in a radiationless transition which forms the second state of the process of light absorption.

1. INTRODUCTION

IN A monatomic gas the transformation of the light energy absorbed by an individual atom into heat, that is into the kinetic energy of the translatory motion, is effected, on the quantum theory, through *a collision of the second kind* of the excited atom with some other (usually unexcited) one. If we now look for the corresponding process in a monatomic solid body, where the heat motion is represented by the vibration of a set of "elastic oscillators" (Debye's waves), we at once meet a grave difficulty. This difficulty consists in the apparent inability of the elastic or heat oscillators, so far as they are assumed to be harmonic and uncoupled with each other, to take up the big quantum of energy stored by the excited atom. This quantum is in fact about 100 times larger than the largest energy quantum of the heat oscillators, corresponding to the ratio between the frequency of the absorbed light and the highest frequency of the heat vibrations. In a radiationless discharge of the excitation energy the latter must therefore be either shared between a great many oscillators, which is impossible if they are uncoupled, or be absorbed by a single oscillator jumping at one time over at least 100 energy levels, which is also impossible if the oscillator is harmonic.

The solution of this difficulty seems at first sight to consist simply in taking account of the actually existing coupling between the different oscil-

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[1] This paper is an extension of two previous ones on the absorption of light in gases: see J. Frenkel, Zeits. f. Physik **58**, 798 (1929) and **59**, 198 (1930).

lators and their nonharmonic character. It must, however, be rejected for it leads to extremely small probabilities for transitions of the type considered. In fact in order to get a non-vanishing probability for a transition involving N elementary jumps, either by N oscillators making each an elementary jump, or by a single oscillator making an N-fold jump, one must carry out the expansion of the potential energy of the oscillators as a function of their coordinates (or of the displacements of the atoms from their equilibrium positions) up to terms of the N-th order at least.[2] The terms one would get for $N \geqq 100$, even if this was practicable, would be hardly large enough to account for the effect we are considering.

There seems to be a less trivial and more successful solution of the above difficulty, which is suggested *by the analogy between a crystal* (*representing a solid body*) *and a molecule.* The usual selection rule for the vibrational quantum number of a molecule (a diatomic molecule, say), restricting its change to unity, holds for such transitions only, for which the electronic state of the molecule remains unaltered. In case however of a combined transition, for instance of a spontaneous transition from an excited state to the normal one with emission of light, the vibrational quantum number can change by any amount (integral, of course) whatever. It may be noted that this "breach" of the selection rule has nothing to do with the possible presence of nonharmonicity, but depends upon the fact that the character of the vibrations in the normal and excited molecule is quite different.

In applying this consideration to a crystal we have only to develop the analogy between an excited crystal and an excited molecule. At the outset we have pictured an excited crystal as differing from the normal one by the presence of one *definite* excited atom. Now in case of a molecule consisting of two identical atoms the excitation cannot be traced to one of them, but has to be considered as a characteristic of the molecule as a whole. The same must be true with respect to a crystal consisting of any number of identical atoms. We thus see that we must first of all revise our conception of an excited crystal by allowing for the identity of all the atoms, and thereafter investigate the influence of the "electronic state" of a crystal on its vibrational states.

2. Excited States of a Crystal; "Excitation-Waves"

We shall assume that the coupling between different—even neighboring—atoms is small compared with the forces holding the electrons within the separate atoms (thus excluding the case of metallic bodies). We shall further suppose that the atoms—or rather the nuclei—are fixed, that is, we shall neglect their vibratory motion, and shall consider only their inner state, characterized by a function of the coordinates of the electrons with respect to the nucleus. Lastly we shall leave out of account the possibility of interchanging the electrons between different atoms and shall consequently assign to a definite atom a definite group of electrons whose coordinates (relative

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[2] See below, Section 4.

to the nucleus) will be represented for the sake of brevity by the number of the respective atom $(1, 2, \cdots, n)$.

Then if ψ_{I} and ψ_{II} are the wave functions representing the normal and the excited state of an *isolated* atom, the stationary states of a system of n atoms, of which one is excited and the rest normal, will be represented to a first approximation by a linear aggregate of n factorial functions,

$$\begin{aligned} \phi_1 &= \psi_{\mathrm{II}}(1)\psi_{\mathrm{I}}(2)\psi_{\mathrm{I}}(3) \cdots \psi_{\mathrm{I}}(n) \\ \phi_2 &= \psi_{\mathrm{I}}(1)\psi_{\mathrm{II}}(2)\psi_{\mathrm{I}}(3) \cdots \psi_{\mathrm{I}}(n) \\ &\cdots\cdots\cdots\cdots\cdots \\ \phi_n &= \psi_{\mathrm{I}}(1)\psi_{\mathrm{I}}(2)\psi_{\mathrm{I}}(3) \cdots \psi_{\mathrm{II}}(n) \end{aligned} \tag{1}$$

with properly chosen coefficients $c_1, c_2, \cdots, c_n$. We have here a particular case of an "exchange degeneracy," which I have already considered previously[3] and which is somewhat similar to the exchange degeneracy met with in the problem of a single electron with n fixed identical nuclei.[4]

There are, as is well known, just n *sets* of coefficients $(c_1, c_2, \cdots, c_n)$, corresponding to the splitting up of the undisturbed state of n isolated atoms with the total energy $W_{\mathrm{II}}+(n-1)W_{\mathrm{I}}$ into n different states, whose energies differ from the preceding value by small amounts W'. These n states will be denoted as the "excitation multiplet" of the crystal. The values of W' for the different components of such a multiplet "$W' = W_r'$) and the corresponding values of the coefficients $c_l (= c_{rl})$ are determined by the equations

$$\sum_{l=1}^{n} U_{kl} c_l = W' c_k \tag{2}$$

where U_{kl} are the matrix elements of the mutual potential energy of all the atoms U with respect to the functions (1).

Now U must reduce to the form

$$U = \sum_{\alpha<\beta} U(\alpha, \beta; R_{\alpha\beta}) \tag{3}$$

where $U(\alpha, \beta; R_{\alpha\beta})$ is the mutual potential energy of the atoms α and β and $R_{\alpha\beta} = R_{\beta\alpha}$ their distance apart (or rather the distance between the respective nuclei). One has obviously $U(\alpha, \beta; R_{\alpha\beta}) = U(\beta, \alpha; R_{\alpha\beta})$. One must not conclude however from this symmetry relation that $U(1, 2, \cdots, n)$ is a symmetrical function of the respective arguments. Interchanging two arguments say 1 and 2—which corresponds eventually to an interchange of the excitation state between the atoms 1 and 2—*we must keep the distances $R_{\alpha\beta}$ fixed*, so that the new energy function obtained by such an interchange is substantially different from the original one.[5]

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[3] Zur Theorie der Resonanzverbreiterung von Spektrallinien, Zeits. f. Physik **59**, 198 (1930).

[4] This problem is treated in Bloch's theory of metallic conductivity.

[5] The theory can be easily extended to account for the interchanging of the electrons between different atoms. In the simplest case of one electron per atom we have but to replace

Taking into account the orthogonality and normality conditions for the functions ψ_{I} and ψ_{II},

$$\int \psi_{\mathrm{I}}(\alpha)\psi_{\mathrm{II}}{}^*(\alpha)d\tau_\alpha = 0, \quad \int \psi_{\mathrm{I}}(\alpha)\psi_{\mathrm{I}}{}^*(\alpha)d\tau_\alpha = \int \psi_{\mathrm{II}}(\alpha)\psi_{\mathrm{II}}{}^*(\alpha)d\tau_\alpha = 1,$$

we easily obtain from (3) if $k \neq l$:

$$U_{kl} = \int \cdots \int U\phi_k{}^*\phi_l \; d\tau_1 \cdots d\tau_n = V_{kl} \tag{4}$$

where V_{kl} is a *function of the distance* R_{kl} *alone* given by

$$V_{kl} = \int \int U(k, l; R_{kl})\psi_{\mathrm{II}}{}^*(k)\psi_{\mathrm{I}}(k)\psi_{\mathrm{I}}{}^*(l)\psi_{\mathrm{II}}(l)d\tau_k d\tau_l \tag{4a}$$

It may be remarked that it is in general complex and therefore different from $V_{lk} = V_{kl}{}^*$.

For $k = l$ we get

$$U_{kk} \equiv V_{kk} = \sum_{l \neq k} \overline{V}_{kl} \tag{5}$$

where

$$\overline{V}_{kl} = \int\int U(k, l; R_{kl}) \,|\, \psi_{\mathrm{II}}(k) \,|^2 \,|\, \psi_{\mathrm{I}}(l) \,|^2 d\tau_k d\tau_l \tag{5a}$$

may be defined as the average value of the mutual energy of the atoms k and l when one of them is in the normal and the other in the excited state. This is also of course a function of the distance R_{kl} only; it is moreover symmetrical with respect to k and l.

The equations (2) are very similar to those which determine the normal modes of vibration of a system of coupled classical oscillators with one degree of freedom each; in fact we have but to consider the coefficients c_k as the amplitudes of these oscillators and to replace the energies W' by the square of the classical frequencies (multiplied by a properly chosen proportionality factor). The matrix elements $U_{kl}(k \neq l)$ can be then interpreted as the coupling coefficients (since they actually depend upon the distance of the

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the functions (1) by the following ones which are antisymmetrical with respect to all the electrons.

$$\phi_1 = \frac{1}{n!^{1/2}} \begin{vmatrix} \psi_{\mathrm{II}}(1, 1), & \psi_{\mathrm{II}}(1, 2), & \cdots \psi_{\mathrm{II}}(1, n) \\ \psi_{\mathrm{I}}(2, 1), & \psi_{\mathrm{I}}(2, 2), & \cdots \psi_{\mathrm{I}}(2, n) \\ \cdots & \cdots & \cdots \\ \psi_{\mathrm{I}}(n, 1), & \psi_{\mathrm{I}}(n, 2) & \cdots \psi_{\mathrm{I}}(n, n) \end{vmatrix} . \quad \phi_2 = \frac{1}{n!^{1/2}} \begin{vmatrix} \psi_{\mathrm{I}}(1, 1), & \psi_{\mathrm{I}}(1, 2) & \cdots & \psi_{\mathrm{I}}(1, n) \\ \psi_{\mathrm{II}}(2, 1), & \psi_{\mathrm{II}}(2, 2) & \cdots & \psi_{\mathrm{II}}(2, n) \\ \cdots & \cdots & \cdots & \cdots \\ \psi_{\mathrm{I}}(n, 1), & \psi_{\mathrm{I}}(n, 2) & \cdots & \psi_{\mathrm{I}}(n, n) \end{vmatrix}.$$

etc. where $\psi_{\mathrm{I}}(k, l)$ and $\psi_{\mathrm{II}}(k, l)$ denote the wave functions of the atom formed by the association of the l-th electron to the k-th nucleus, in the normal and excited state respectively. Similar, though somewhat more complicated, results are obtained in the general case of several electrons per atom.

The case of two electrons with all the atoms being in the normal state has been recently treated by E. Hylleraas, Zeits. f. Physik **63**, 771 (1930) in connection with the theory of the cohesive forces in a (non-excited) crystal of sodium hydride.

respective oscillators only), and the U_{kk} as the coefficients of the quasi-elastic forces for the uncoupled oscillators.

Until now the positions of the atoms have remained unspecified. We shall now assume that the nuclei are fixed at the lattice points of the crystal, neglecting the displacements due to the vibratory motion. We shall further assume that the crystal has a rectangular form (or the form of a parallelepiped whose edges are parallel to the crystalline axes). The normal modes of vibration for this case are well known. They do not depend upon the shape of the functions $V_{kl}(R_{kl})$ nor upon the value of the constant $V_0 = V_{kk}$, thus coinciding with respect to the position of the nodal planes with the acoustic or elastic vibrations (for which $V_0 = 0$). These vibrations can be described as *standing waves* with the wave-number components[6]

$$g_1 = \pm r_1/2a_1, \quad g_2 = \pm r_2/2a_2, \quad g_3 = \pm r_3/2a_3 \tag{6}$$

where a_1, a_2, a_3 are the edges of the crystal and r_1, r_2, r_3 numbers specifying the mode of normal vibrations and taking all integral values between 0 and $n_1 - 1$, $n_2 - 1$, $n_3 - 1$, respectively, n_i being the number of atoms along the i-th edged ($n = n_1 n_2 n_3$).

The triplet ($r_1 r_2 r_3$) replaces the number r which was introduced to specify the various solutions of the equations (2). The single numbers k and l must be replaced accordingly by triplets ($k_1 k_2 k_3$), ($l_1 l_2 l_3$) which may be associated with definite "oscillators," that is definite atoms of the lattice. It may be remarked that the coefficient c_k in (2) refers to that function ϕ_k in (1) which ascribes the excited state to the atom k. The solutions of the equations (2) can now be put in the form

$$c_{r_1, r_2, r_3; k_1, k_2, k_3} = A_{r_1 r_2 r_3} \cos \frac{\pi\delta}{a_1} k_1 r_1 \cos \frac{\pi\delta}{a_2} k_2 r_2 \cos \frac{\pi\delta}{a_3} k_3 r_3 \tag{7}$$

where δ is the lattice constant (for the sake of simplicity the lattice will be pictured as cubical), and $k_1\delta = x_1$, $k_2\delta = x_2$, $k_3\delta = x_3$ the rectangular coordinates of the atom to which the excited state is assigned by the function $\phi_{k_1 k_2 k_3}$. $A_{r_1 r_2 r_3}$ is a normalization coefficient determined by the condition that the integral of the square of the function

$$\chi_{r_1 r_2 r_3}(1, 2, \cdots n) = \sum_{k_1 k_2 k_3} c_{r_1, r_2, r_3; k_1, k_2, k_3} \phi_{k_1 k_2 k_3}(1, 2, \cdots n) \tag{7a}$$

representing the r-th stationary state of the excited crystal (the r_1, r_2, r_3 component of the "excitation multiplet") over the configuration space of all the electrons should be equal to 1.

The energies $W'_{r_1 r_2 r_3}$ of the different states (with respect to the unperturbed energy $W_{\rm II} + (n-1) W_{\rm I}$) are given directly by substituting in the equations (2) the values (7) of the coefficients c. Since the matrix elements U_{kl} depend only upon the differences $k_1 - l_1$, $k_2 - l_2$, $k_3 - l_3$ one can put $k_1 = k_2 = k_3 = 0$ which gives

$$A_r W_r' = \sum_l U_{0l} c_{rl}$$

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[6] The wave number is the reciproal of the wave-length; it is a vector parallel to the direction of the propagation of the waves.

or more fully written

$$W'_{r_1r_2r_3} = \sum_{l_1} \sum_{l_2} \sum_{l_3} U_{000,l_1l_2l_3} \cos \frac{\pi\delta}{a_1} l_1 r_1 \cos \frac{\pi\delta}{a_2} l_2 r_2 \cos \frac{\pi\delta}{a_3} l_3 r_3 \tag{8}$$

With increasing values of $l_1l_2l_3$, that is with increassing distance $R_{0l} = \delta(l_1^2 + l_2^2 + l_3^2)^{1/2}$, the values of $H'_{000l_1l_2l_3}$ must in general decrease very rapidy. The summation in (8) can be therefore extended practically over all values of the l_i from $-\infty$ to $+\infty$. If the mutual action of neighboring atoms only (with smallest distance apart $R = \delta$) is taken into account, (8) reduces to

$$W'_{r_1r_2r_3} = V_0 + 2V_1\left(\cos \frac{\pi\delta}{a_1} r_1 + \cos \frac{\pi\delta}{a_2} r_2 + \cos \frac{\pi\delta}{a_3} r_3\right) \tag{8a}$$

where V_1 is the value of (4a) for neighboring atoms and V_0 six times the value of (5a) for the same atoms. The latter value is the average of the mutual potential energy between an excited and an unexcited atom, whereas V_1 has the character of an "exchange energy" which has no classical analogue.

Each stationary state of an excited crystal can be described as a "standing excitation wave" defined by (7) or by

$$c(x_1x_2x_3) = A \cos 2\pi g_1 x_1 \cos 2\pi g_2 x_2 \cos 2\pi g_3 x_3 e^{-2\pi i \nu' t}$$

where $\nu' = W'_r/h$, $x_i = \delta l_i$. Such a standing wave can be obtained by superposing eight "progressive excitation waves" of the type

$$(A/8)e^{2\pi i(g_1x_1 + g_2x_2 + g_3x_3 - \nu' t)}$$

which represent the propagation of the probability for finding the excitation localized in a certain plane of the crystal. By superposing a number of such waves with slightly different values of g_1, g_2, g_3 (that is with slightly different directions of propagation and frequencies $\nu' = w'/h$) it is always possible to construct a wave-packet which will represent the excitation being concentrated in a definite atom or its neighborhood (according to the usual picture). The group velocity of such an "excitation-packet" may be determined by the relations

$$v_i = \partial\nu'/\partial g_i (i = 1, 2, 3). \tag{9}$$

Putting

$$h\nu' = V_0 + 2V_1(\cos 2\pi g_1\delta + \cos 2\pi g_2\delta + \cos 2\pi g_3\delta)$$

according to (8a) and (6), we get

$$v_i = -\frac{4\pi\delta V_1}{h} \sin 2\pi g_i\delta. \tag{9a}$$

For small values of g_i that is for long "excitation waves" this expression reduces to

$$v = -\frac{8\pi^2\delta^2 V_1}{h} g \tag{9b}$$

that is the group velocity is approximately proportional to the wave number. It has in general the same direction so long as the "exchange energy" V_1 is negative. It reaches its maximum value $v \cong 4\pi\delta \mid V_1 \mid / h$ for wave-lengths equal approximately to four times the interatomic distance δ. For $\lambda \cong 2\delta$ it falls down to zero and for still shorter wave-lengths becomes opposite to the direction of the wave propagation.[7]

To get a better understanding of the nature of the "excitation waves" it will be well to consider the process corresponding to them in the older quantum theory and in the classical theory. According to the former the exitation energy of an atom can and in fact must be transmitted to one of the other atoms of the same sort either by emission and (resonance) reabsorption, of light or directly in a non-radiative process. The closer the atoms are together, the larger must be the probability of such a non-radiative transmission, that is, the larger the velocity with which the "excited state" will travel from one place to the other. This is expressed by the fact that the group velocity, according to (9a), is proportional to the exchange energy V_1. The ratio $\delta / v_{\max}$ which is of the order of magnitude of h / V_1 can be considered as the shortest time that the excitation remains confined to one definite atom.[8]

From the point of view of the classical theory an atom has to be considered as a harmonic oscillator, whose normal state is that of rest. The energy of the free oscillations, replacing the excitation energy, instead of being concentrated in one single atom (or a small number of them in the general case) has to be distributed here in a more or less uniform manner over all the atoms, each of them possessing accordingly but a very small energy. The excitation waves can be represented in this case by the familiar waves of the electric polarization with exactly the same wave-numbers as has been actually done above in the discussion of the equation (2).[9] It should be noticed however that in the classical theory of the propagation of such waves the interaction between the atoms is considered to be a radiative one, that is proportional to their dipole moment and inversely proportional to the distance, whereas in the wave mechanical theory we are developing this interaction considered as a much more powerful non-radiative (electrostatic) one.[10]

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[7] These results are wholly analogous to those implied in Bloch's theory of the electrical conductivity of metals and discussed by R. Peierls.

[8] In case of two atoms h / V_1 is just equal to the time in which the excited state oscillates from one atom to the other.

[9] The situation becomes more complicated if instead of one excited atom we consider the case of two or more excited atoms. cf. J. Frenkel, Zeits. f. Physik **59**, 198 (1930) in particular footnote on p. 203.

[10] Cf. G. Breit and E. O. Salant, Phys. Rev. **36**, 871 (1930). This paper dealing with the propagation of light in solids contains some results of the present section.

3. The Influence of Excitation on the Geometric and Elastic Properties of a Crystal and its Vibratory Motion

We can now turn to the examination of the influence which an excited state of a crystal (that is a definite component of an excitation multiplet) exerts upon the heretofore neglected vibratory motion of the atoms. The exact way to deal with this question would be to consider simultaneously the "inner" and the "outer" (that is, vibratory) motion of the atoms. But this way is hardly practicable even in the simplest case of a diatomic molecule, and we shall therefore use an approximate method of the same sort which is applied in Debye's theory of specific heats to the determination of the normal vibrations corresponding to the unexcited state.

A normal vibration is described here by a system of standing sound waves of just the same geometrical type as that used in the preceding paragraph to describe the excitation states. It can be thus characterized by specifying the components of the wave-number according to the equations (6) which we shall rewrite in the form

$$g_1' = \pm r_1'/2a_1, \quad g_2' = \pm r_2'/2a_2, \quad g_3' = \pm r_3'/2a_3 \tag{10}$$

the primes serving to distinguish the sound waves from the excitation waves.[11]

The frequency of the vibrations ν' can be determined from the equation

$$\nu' = g'u \tag{11}$$

where u denotes the *velocity of sound*, which is considered as independent of g'. The velocity of sound can be calculated by means of the formula

$$u = (\kappa/\rho)^{1/2}$$

where ρ is the density of the crystal, and κ its elastic modulus, which has different values for the longitudinal and the transverse vibrations.

Now in order to determine κ from atomic data we must consider the vibrationless state of the crystal and compare its energy in the equilibrium state with the energy corresponding to a slightly compressed (or expanded) state in the case of κ_{long} or to a slightly distorted state in the case of κ_{trans}.

Denoting the volume of the crystal with v and its energy—that is the mutual potential energy of all its atoms—in the normal (non-excited) state with W_0 we have, expanding W_0 in a power series with respect to the increment of volume $v-v^0$ ($v^0=v$ in the equilibrium state)

$$W_0 = W_0^0 + \frac{1}{2}\left(\frac{\partial^2 W_0}{\partial v^2}\right)^0 (v - v^0)^2.$$

The second term represents the elastic energy

$$\tfrac{1}{2}\,\kappa_0(v-v^0)^2 \cdot v^0$$

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[11] We shall drop the primes later on when there will be no danger of confusing the sound waves with the excitation waves.

whence it follows

$$\kappa_0 = v_0^0\left(\frac{\partial^2 W_0}{\partial v^2}\right)$$

or putting $v = n\delta^3$

$$\kappa_0 = \frac{\delta_0^2}{9}\,\frac{1}{v_0^0}\left(\frac{\partial^2 W_0}{\partial \delta^2}\right)^0 = \frac{1}{9n\delta_0}\left(\frac{\partial^2 W_0}{\partial \delta^2}\right)^0. \tag{13}$$

This formula determines the modulus of compressibility for the normal (unexcited) state of the crystal—as denoted by the subscript zero—and hence according to (12) and (11)[12] the frequency of the vibrations associated with this state. It may be remarked that the corresponding equilibrium value of $\delta = \delta_0^0 = \delta_0$ is given by the equation $(\partial W_0/\partial v)^0 = 0$ or

$$(\partial W_0/\partial \delta)^0 = 0 \tag{13a}$$

and that δ_0 is related to the density $\rho = \rho_0$ by means of

$$\rho_0 = m/\delta_0^3 \tag{13b}$$

m being the mass of an atom.

The above method can now obviously be applied to the determination of the vibrations associated with an excited state of the crystal. To do this we have but to replace in the preceding formulae the energy W_0 by the energy $W_r = W_0 + W'_r$ of one of the components of the excitation multiplet. In this way we shall get for the lattice constant of the crystal δ_r its density ρ_r and its elastic modulus κ_r values depending upon the character of the excitation substate and slightly different from those corresponding to the normal one.

Since the difference $\delta_r - \delta_0 = \Delta\delta_r$ is very small, we have to a first approximation

$$\left(\frac{\partial W_r}{\partial \delta_r}\right)^0 = \left(\frac{\partial W_0}{\partial \delta}\right)_{\delta=\delta_0} + \left(\frac{\partial^2 W_0}{\partial \delta^2}\right)_{\delta=\delta_0}\Delta\delta_r + \left(\frac{\partial W_r'}{\partial \delta}\right)_{\delta=\delta_0} = 0,$$

whence since the first term vanishes (according to 13a)

$$\Delta\delta_r = -\frac{\partial W_r'}{\partial \delta}\Big/\frac{\partial^2 W_0}{\partial \delta^2}\quad(\delta = \delta_0) \tag{14}$$

The energy W_0 is proportional to the number of atoms n, whereas W'_r according to (8) or (8a) depends upon it in a practically unimportant way. Putting in (8a)

$$a_1 = n_1\delta,\quad a_2 = n_2\delta,\quad a_3 = n_3\delta$$

(where $n_1n_2n_3 = n$) we have

$$W_r' = V_0 + 2V_1\left(\cos\frac{\pi r_1}{n_1} + \cos\frac{\pi r_2}{n_2} + \cos\frac{\pi r_3}{n_3}\right) \tag{15}$$

and consequently

$$\Delta\delta_r = -\frac{\partial V_0}{\partial \delta}\Big/\frac{\partial^2 W_0}{\partial \delta^2} - 2\left(\cos\frac{\pi r_1}{n_1} + \cos\frac{\pi r_2}{n_2} + \cos\frac{\pi r^3}{n_3}\right)\frac{\partial V_1}{\partial \delta}\Big/\frac{\partial^2 W_0}{\partial \delta^2} \tag{15a}$$

which is of the order of magnitude of $1/n$, since V_1 does not depend upon n.

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[12] In the case of longitudinal vibrations.

In the same way we get from (13)

$$\Delta\kappa_r = \kappa_r - \kappa_0 = \frac{2}{9\delta n}\left[\frac{\partial^2 V_0}{\partial\delta^2} + 2\left(\cos\frac{\pi r_1}{n_1} + \cos\frac{\pi r_2}{n_2} + \cos\frac{\pi r_3}{n_3}\right)\right]\frac{\partial^2 V_1}{\partial\delta^2}\cdot \qquad (15b)$$

The relative change of $\Delta\kappa_r$ being again of the order of magnitude of $1/n$.

These results seem very natural indeed. We should expect that the change of the geometric and dynamic properties of the crystal lattice, due to the excitation of a few atoms n' depends upon their *relative* number, that is upon the ratio n'/n, which in our case is equal to $1/n$. So long as n' is small compared with n the effects due to the excitation of the separate atoms must obviously behave additively (which would no longer be the case if n' were comparable with n), so that to get the total change of δ or κ we would have but to add the expressions (15a) or (15b) for all the n' excited atoms. It seems however that even with the largest values of n' that can be obtained by illuminating the crystal with intense light of the resonance frequency, the change in the elastic properties will be too minute to be detected by direct measurement.

This change must however manifest itself in an indirect manner by making possible the radiationless transitions of the crystal from an excited state into the normal one with conversion of the excitation energy into that of the vibrational motion, and also of course transitions of the inverse direction, leading to "thermal excitation" of the crystal and corresponding to "inelastic collisions of the first kind" or "activating collisions" in the case of a gas.

4. THE RELATION BETWEEN THE VARIABLES AND FUNCTIONS DESCRIBING THE HEAT OSCILLATORS IN THE NORMAL AND THE EXCITED CRYSTAL

In order to determine the probability of such transitions we must introduce first of all the "normal coordinates" characterizing the individual heat oscillators, which represent the different modes of vibration (standing elastic waves) of the crystal. Let these coordinates for the unexcited state be denoted by $\xi_1, \xi_2, \cdots \xi_n \cdots \xi_{3n}$ (their number being equal to the number of degrees of freedom); we shall think of the first n as referring to the longitudinal vibrations and the rest to transverse ones.

We have to introduce in the second place the relations between these coordinates and the normal coordinates $\xi_{r1}, \xi_{r2}, \cdots$ which correspond to the r-th excited state. These relations must be derived from the condition that the equilibrium positions of the atoms in the excited state are specified by zero values of the new coordinates ($\xi_{rs}=0$) on the one hand and by definite non-vanishing values $\xi_s = \xi_s{}^r$ of the old ones on the other.

For the sake of simplicity we shall limit ourselves to the consideration of a *unidimensional* case, that is of a set of n atoms situated on a straight line and capable of moving along this line (that is to perform longitudinal oscillations). Such a set can be conveniently treated as a "bar." In order to allow for the change of length $L=\delta n$ of the bar, due to the excitation of one of its atoms we shall imagine one of its ends to be fixed and the other free.[13] The normal modes of vibration of such a bar correspond to wave-lengths $\lambda = \lambda_l$ determined by the equation

$$L = \frac{2l+1}{4}\lambda_l = n\delta \tag{16}$$

where $l=0, 1, 2, \cdots n-1$. The displacement Δx_k of an atom whose equilibrium distance from the fixed end is $x_k = k\delta$ can be represented by the sum

$$\Delta x_k = \sum_{l=0}^{n-1} c_{kl}\xi_l \tag{17}$$

where

$$c_{kl} = \gamma \sin \frac{2\pi x_k}{\lambda_l} = \gamma \sin \frac{\pi}{n}\left(l + \frac{1}{2}\right)k \tag{17a}$$

γ being determined by the "normality condition"

$$\sum_{k=0}^{n-1} c_{kl}^2 = 1 \tag{17b}$$

and ξ_l denoting the normal coordinate, which characterizes the l-th mode of vibration.

Using the formula

$$\sum_{k=0}^{n-1} e^{i\alpha k} = \sum_{k=0}^{n-1} \cos \alpha k + i \sum_{k=0}^{n-1} \sin \alpha k = \frac{1 - e^{i\alpha n}}{1 - e^{i\alpha}}$$

which is equivalent to

$$\sum_{k=0}^{n-1} \mathrm{cs}\, \alpha k = \frac{1 + \cos \alpha(n-1) - \mathrm{cs}\, \alpha n - \mathrm{cs}\, \alpha}{2(1 - \mathrm{cs}\, \alpha)} = \frac{1}{2}(1 - \mathrm{cs}\, \alpha n) + \frac{\mathrm{sn}\, \alpha n\, \mathrm{sn}\, \alpha}{2(1 - \mathrm{cs}\, \alpha)}$$

$$\sum_{k=0}^{n-1} \mathrm{sn}\, \alpha k = \frac{\sin \alpha(n-1) - \sin \alpha n + \sin \alpha}{2(1 - \mathrm{cs}\, \alpha)} = -\frac{1}{2} \sin \alpha n + \frac{\mathrm{sn}\, \alpha(1 - \mathrm{cs}\, \alpha n)}{2(1 - \mathrm{cs}\, \alpha)},$$

we get with the abbreviations $(l+\frac{1}{2})\pi/n = \beta$, $(l'+\frac{1}{2})\pi/n = \beta'$

$$\sum_{k=0}^{n-1} c_{kl}c_{kl'} = \gamma^2 \sum_{k=0}^{n-1} \sin \beta k \sin \beta' k = \frac{1}{2}\gamma^2 \left[\sum_{k=0}^{n-1} \mathrm{cs}\, (\beta - \beta')k - \sum_{k=0}^{n-1} \mathrm{cs}\, (\beta + \beta')k \right]$$

$$= n - 1 \text{ if } l' = l \text{ and } (-1)^{l \pm l' + 1} \text{ if } l' = l.$$

We thus see that

$$\gamma = (n-1)^{-1/2}$$

and morever that the coordinates ξ_l are *not exactly* orthogonal as they would be in the limiting case $n \to \infty$, $n\delta = L = \text{const.}$

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[13] Similar results would be obtained by fixing the middle point of the bar and leaving both ends free and in the opposite phase.

Squaring (17) and summing up with respect to k we have in fact:

$$\sum_{k=0}^{n-1}(\Delta x_k)^2 = \sum_{l=0}^{n-1}\xi_l^2 - \frac{2}{n-1}\sum_{l<l'}(-1)^{l'-l}\xi_l\xi_l{}'.$$

The mutual potential energy of the atoms which in the simplest case is represented by the sum

$$\sum_{k=0}^{n-2}(\Delta x_{k+1} - \Delta x_k)^2$$

also will not be reduced exactly to a sum of squares of the type

$$2\pi^2\sum_{l=0}^{n-1}\nu_l^2\cdot\xi_l^2$$

ν_l being the vibration frequencies, but will contain cross terms vanishing in the limiting case of a continuous bar. The problem of finding the exact normal coordinates that is the exact transformation coefficients c_{kl} in the equations (17) for a given finite value of n is rather complicated and we shall therefore use the "nearly-normal" coordinates defined above.

Since the coefficients c_{kl} do not depend upon the equilibrium spacing between the atoms δ, the same formulae (17) could be used both for the "normal" and for the "excited" bar; it should be remembered however that Δx_k has in both cases a different meaning, the equilibrium position of the k-th atom in the excited state being displaced by $\Delta\delta_r k$ with respect to that corresponding to the normal state. The same position of the atoms which in the normal state is specified by the displacements (17) will be specified from the point of view of the excited state r by the displacements

$$\Delta x_{rk} = \Delta x_k - k\Delta\delta_r = \sum c_{kl}\xi_{rl}$$

whence

$$\sum_{l=0}^{n-1}c_{kl}(\xi_{rl} - \xi_l) = -k\Delta\delta_r.$$

If c_{kl} were the correct transformation coefficients then these equations would be immediately solved by

$$\xi_{rl} - \xi_l = \Delta\xi_{rl} = -\sum_{k=0}^{n-1}c_{kl}k\Delta\delta_r.$$

Introducing here the approximate values

$$c_{kl} = \frac{1}{(n-1)^{1/2}}\sin\frac{\pi}{n}\left(l + \frac{1}{2}\right)k$$

we have

$$\Delta\xi_{rl} = -\frac{\Delta\delta_r}{(n-1)^{1/2}}\sum_{k=0}^{n-1}k\sin\alpha k$$

or

$$\Delta\xi_{rl} \cong \frac{\Delta\delta_r}{n^{1/2}}\left(\frac{\partial}{\partial\alpha}\sum_{k=0}^{n-1}\cos\alpha k\right)_{\alpha=\pi/n(l+1/2)}$$

that is according to the summation formula given above, with $\cos \alpha n = 0$, $\sin \alpha n = (-1)^l$,

$$\Delta\xi_{rl} = (-1)^l \frac{\Delta\delta_r}{2n^{1/2}} \left[n - \frac{1}{1 - \mathrm{cs}\ \alpha} \right].$$

The second term in the brackets represents probably the error due to the fact that we have been using inexact values for the coefficients c_{kl}. It would have an important influence only in the case of very small values of α corresponding to very long waves.[14]

Dropping it we get finally

$$\Delta\xi_{rl} = (-1)^l \frac{1}{2} \Delta\delta_r n^{1/2} = (-1)^l \frac{1}{2} \frac{\Delta L_r}{n^{1/2}} \tag{18}$$

where $\Delta L_r = n\Delta\delta_r$ denotes the change of length of the whole bar in the r excited state. Since this change is actually due to the presence of one single excited atom, it must be practically independent of the total number of atoms, whence it follows that $\Delta\delta_r$ must be inversely proportional to n, a result which we have derived above from somewhat different considerations for the case of the real three-dimensional crystal. The preceding formula which we can safely extend to this case[15] thus means that the change of the normal coordinates, produced by the excitation of one atom out of n is inversely proportional to the *square root* of n. The coefficient of proportionality $\frac{1}{2}\Delta\delta_r n$ is determined by (15a) and can be shown to be of the order of magnitude of atomic dimensions.

Having established the relation between the normal coordinates of the nonexcited and those of the excited crystal we must now turn to the consideration of the Schrödinger wave functions of the corresponding "heat oscillators." These functions will be denoted by $f_{s,N_s}{}^0(\xi_s)$ for the N_s quantum state of the s-th oscillator in the case of the unexcited crystal and by $f_{s,N_s}{}^r(\xi_{rs})$ in the case of a crystal in the r-th state of an excitation multiplet. The general form of the functions $f_N(\xi)$ is given by the formula

$$f_N(\xi) = [2^N N!(\pi\alpha)^{1/2}]^{-1/2} H_N(\alpha^{1/2}\xi) e^{-1/2\alpha\xi^2} = f_N{}^*(\xi) \tag{19}$$

where H_N is Hermite's polynomial of the N-th degree and α is a constant proportional to the natural frequency of the oscillator ν. If the coordinate ξ is normalized in such a way that the energy of the oscillator is represented by

$$\frac{m}{2}\left[\left(\frac{d\xi}{dt}\right)^2 + 4\pi^2\nu^2\xi^2\right]$$

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[14] In this case we should have

$$1 - \cos \alpha \cong \tfrac{1}{2}\alpha^2 = (l + \tfrac{1}{2})^2 \pi/2n^2$$

and

$$c_{kl} \cong (-1)^l \frac{\Delta\delta_r}{n^{1/2}} \frac{n^2}{\pi^2(l + \frac{1}{2})^2}$$

[15] Replacing l by the sum $l_1 + l_2 + l_3$.

then[16]

$$\alpha = 4\pi^2 m\nu/h. \tag{19a}$$

The absolute value of α does not play any role since we can always replace the coordinate ξ by $\eta = \alpha^{1/2}\xi$. If however we have to compare the behavior of the same oscillator for two different values of the frequency parameter $\nu = \nu_0$ and $\nu = \nu_r$ then we must take into account the relative value of α which gives us two different wave functions of the form

$$f_N{}^0(\xi_1) = f_N(\xi_1) \text{ and } f_N{}^{(r)}(\xi_r) = f_N\left[\left(\frac{\nu_{rs}}{\nu_{0s}}\right)^{1/2}\xi_{rs}\right]. \tag{20}$$

The function $f_N(\xi)$ can be defined here and in the sequel by formula (5) with $\alpha = 1$.

5. DETERMINATION OF THE PROBABILITY OF THE INDIVIDUAL TRANSITIONS OF A CRYSTAL FROM THE EXCITED TO THE NORMAL STATE (or *vice versa*).

The stationary states of the crystal, including the vibratory motion of the atoms can be described to a first approximation by a wave function Ψ equal to the product of an electronic function $\chi(1, 2 \cdots n)$ specifying the inner states of the atoms and of the functions (20) for all the $3n$ oscillators. We thus get for the r-th excited substate

$$\Psi_r = \chi_r(1, 2, \cdots n) \prod_{s=1}^{3n} f_{N_{rs}}\left[\left(\frac{\nu_{rs}}{\nu_{0s}}\right)^{1/2}\xi_{rs}\right] \tag{21}$$

and for the normal state

$$\Psi_0 = \chi_0(1, 2, \cdots n) \prod f_{N_{0s}}(\xi_s) \tag{22}$$

with

$$\chi_0 = \psi_1(1)\psi_1(2) \cdots \psi_1(n) \tag{22a}$$

which is obviously the same approximation to the electronic function of a number of atoms in the same state, as the functions χ_r defined by (8), are for the case when one of them is excited.

It must be remarked that whereas the factorization of the oscillator functions corresponds to the assumed absence of any direct coupling between them, the multiplication of these functions with the electronic function χ does not mean that there is no coupling between the vibratory and inner motion of the atoms, this coupling being in fact expressed (in an approximate manner of course) by the dependence of the vibration frequencies ν_{rs} upon the electronic state. Through this interaction of the electronic (inner) and the vibratory (outer) motion the different oscillators are actually coupled with each other—in a rather indirect way—and it is just this indirect coupling that enables the simultaneous transition of any number of oscillators

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[16] Cf. A. Sommerfeld, Wellenmechanisches Ergänzungsband, p. 18. This normalization corresponds to the condition $\Sigma\xi_s{}^2 = \Sigma(\Delta\chi)_s{}^2$ or $\Sigma_l c_{kl}{}^2 = 1$ used above.

from one state, specified by the quantum numbers N_{01}, $N_{02} \cdots N_{03n}$ to another N_{r1}, $N_{r2} \cdots N_{r3n}$, if this transition is combined with an electronic one, that is with a transition of the crystal from the normal state to an excited one or *vice versa.*

The probability of such a combined transition is determined by the matrix element of the perturbation energy with respect to the functions (21) and (21a). This perturbation energy seems at first sight to be identical with the mutual potential energy of all the atoms U, which has been considered above in connection with its influence on the electronic motion. It will be remembered however, that this influence has been examined on the assumption that the atoms were at rest at the lattice points of the crystal, which corresponds to definite equilibrium values $R_{\alpha\beta}{}^0$ of the interatomic distances $R_{\alpha\beta}$ entering as parameters in the expression (3) for U.

Since we are now concerned with transitions due to the interaction of the electronic and vibratory motion it is necessary to take account of the change of the $R_{\alpha\beta}$'s and consequently of U which are due to the displacements of the atom from their equilibrium positions. This could be done by expanding U in a power series with respect to the differences $R_{\alpha\beta} - R_{\alpha\beta}{}^0$ and expressing the latter through the normal coordinates $\xi_1, \xi_2 \cdots \xi_{3n}$.

The series so obtained would contain next to the equilibrium value of U a sum of squares of the coordinates ξ which must be dropped out, since it represents nothing else but the potential energy of the oscillators (accounted for separately) and further higher powers of the ξ's which should represent a certain degree of anharmonicity and of direct coupling between the oscillators and at the same time a certain alteration of the electronic states as a result of the vibrational motion.

If we did not take into account the indirect coupling (and anharmonicity) expressed by the dependence of the vibration frequencies on the excitation state, we should have to carry out the expansion of U up to terms of the 100-th (or even higher) degree in the ξ's in order to get a nonvanishing probability for transitions involving a 100-fold jump of the oscillators (cf. Introduction). As a matter of fact, however, this is not necessary and we can safely stop at terms of the third order (as is done in the theory of the thermal expansion and thermal conductivity of solids) thus putting

$$U = U^0 + U''' \tag{23}$$

where

$$U''' = \sum_{k,l,m} A_{klm}\xi_k\xi_l\xi_m \tag{23a}$$

the coefficients A_{klm} being certain functions of the electronic (inner) coordinates $1, 2, \cdots n$.

The probability of radiationless transitions from the r-th excited state to the normal one (or *vice versa*) is determined by the matrix element of U with respect to the wave functions (21) and (22)

$$M_r \equiv \int U\psi_0{}^*\psi_r = \int \cdots \int \cdots \int U\chi_0{}^*\chi_r d\tau_1 \cdots d\tau_n$$

$$\cdot \prod_{s=1}^{3n} f_{N_{0s}}(\xi_s) f_{N_{rs}}\left[\left(\frac{\nu_{rs}}{\nu_{0s}}\right)^{1/2} \xi_s\right] d\xi_s .$$

Of course only such states have to be considered which have the same or nearly the same energy (the corresponding transitions are usually denoted as "resonance" ones). The energy of the crystal in the normal state is equal to the sum of the energies of the separate atoms nW_I plus the equilibrium value of their mutual potential energy

$$\begin{aligned} W_0' &= \int \cdots \int U(\chi_0)^2 d\tau_1 \cdots d\tau_n \\ &= \sum_{\alpha<\beta} \int\int V(\alpha, \beta; R_{\alpha\beta}) \mid \psi_{\mathrm{I}}(\alpha) \mid ^2 \mid \psi_{\mathrm{I}}(\beta) \mid ^2 d\tau_\alpha d\tau_\beta \end{aligned} \tag{25}$$

plus the vibrational energy

$$E_0 = \sum_{s=1}^{3n} h\nu_{0s}(N_{0s} + \tfrac{1}{2}). \tag{25a}$$

The energy of the same crystal in the excited state r is represented similarly by the sum

$$W_{\mathrm{II}} + (n-1)W_{\mathrm{I}} + W_r' + E_r$$

where W_r' is given by (8) and

$$E_r = \sum_{s=1}^{3n} h\nu_{rs}(N_{rs} + \tfrac{1}{2}). \tag{25b}$$

The condition for the radiationless transition to be a resonance one is thus expressed by the equation

$$W_{\mathrm{II}} - W_{\mathrm{I}} + W_r' - W_0' + \sum_{s=1}^{3n} [h\nu_{rs}(N_{rs} + \tfrac{1}{2}) - h\nu_{0s}(N_{0s} + \tfrac{1}{2})] = 0. \tag{26}$$

This equation can be approximately satisfied for a given r in a number of different ways corresponding to different jumps of the vibrational quantum numbers n_s. The total probability for the crystal to pass from the excited state into the normal one will be proportional to the sum of the squares of the matrix elements (24) (or rather their moduli) for all such "nearly resonance" transitions (see next paragraph).

In computing the matrix elements (24) we must express the normal coordinates of the excited crystal through those of the unexcited one by means of the relation (18). It is however to be kept in mind that these relations hold for the case when the ξ_s's are so normalized that $\Sigma_s \xi_s{}^2 = \Sigma \Delta x_s{}^2$, which corresponds to the value (19a) of the parameter α in the functions (19). If we put

$\alpha=1$ in (19), that is replace ξ_s by $\alpha^{1/2}\xi_s$ then in using the relations (18) we must multiply the right hand side by $\alpha^{1/2}$. Putting further $\nu_r/\nu_0=1+\Delta\nu_r/\nu_0$ and noticing that $\Delta\nu_r/\nu_0$ is a small quantity of the order of $1/n$ we can expand $f_N[(\nu_r/\nu_0)^{1/2}\xi_{rs}]=f_N[(\nu_r/\nu_0)^{1/2}(\xi_s+\Delta\xi_{rs})]$ in a series of powers of $1/n^{1/2}$

$$f_N[(\nu_r/\nu_0)^{1/2}\xi_{rs}] = f_N(\xi_s) + \Delta\xi_{rs}f_N'(\xi_s) + O(1/n) \tag{27}$$

$O(1/n)$ denoting the sum of terms of the order of magnitude $1/n$, $1/n^{3/2}$, etc. We shall presently see that all these terms can be dropped, their contribution to the total value of the transition probability (for all the possible individual transitions) decreasing with increase of n (as $1/n$ at least), whereas the contribution of the terms proportional to $\Delta\xi_{rs}$ that is to $1/n^{1/2}$ turns out to be independent of n (see below).

The change of the vibration frequencies connected with the excitation of the crystal is thus immaterial for the transitions we are considering, these transitions being due practically solely to the minute change of the equilibrium distance between the atoms.[17]

We shall first consider that part of M_r which corresponds to U^0 that is

$$M_r{}^0 = \int\cdots\int U^0\chi_0{}^*\chi_r d\tau_1\cdots d\tau_n \prod_{i=1}^{3n}\int f_{N_{0s}}(\xi_s)f_{N_{rs}}[(\nu_{rs}/\nu_{0s})^{1/2}\xi_{rs}]d\xi_s. \tag{28}$$

The contribution of each oscillator to $M_r{}^0$ is given according to (27) by the factor

$$I_r = \int f_{N_0}(\xi)f_{N_r}(\xi)d\xi + \Delta\xi_r\int f_{N_0}(\xi)f'_{N_r}(\xi)d\xi + O(1/n). \tag{29}$$

If $N_r=N_0$, this factor reduces practically to 1. If $N_r=N_0\pm1$ the first term on the right side vanishes but the second is different from zero, so that $I_r=O(1/n^{1/2})$. If $|N_r-N_0|>1$ the second term vanishes too and I_r turns out to be of the order of $1/n$ or still smaller.

We thus see that *only such transitions have to be taken into account, for which each oscillator either remains in the same state or jumps to the next one.*

From the well-known relation for Hermitian polynomials

$$\frac{d}{d\xi}H_N(\xi) = 2NH_{N-1}(\xi)$$

it follows, according to (19) (with $\alpha=1$):

$$f_N'(\xi) = (2^N N!\pi^{1/2})^{-1/2}2NH_{N-1}(\xi)e^{-\xi^2/2} - \xi f_N(\xi) = (2N)^{1/2}f_{N-1}(\xi) - \xi f_N(\xi)$$

whence for $N_r=N_0\pm1$

$$I_r = -\Delta\xi_r\int f_{N_0}(\xi)f_{N_r}(\xi)\xi d\xi = -\Delta\xi_r\xi_{N_r,N_0}$$

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[17] This result applies to some extent to the case of diatomic molecules, where however the frequency shift also plays a marked rôle.

ξ_{N_r, N_0} being the matrix element of ξ. This matrix element is equal to $(N/2)^{1/2}$ where N is the larger of the two numbers N_r and N_0. We thus get for the s-th oscillator ($\Delta\xi_r$ being independent of s)

$$I_{rs} = -\Delta\xi_r(N_s/2)^{1/2} \quad (N_s = N_{0s}, N_{rs} \text{ if } N_{0s} = N_{rs} = \pm 1). \tag{29a}$$

(The same result can be derived directly from the well-known formula for the matrix element of the momentum, that is of the operator $(h/2\pi i)\,\partial/\partial\xi$). Hence it follows that in case of a transition in which p of the $3n$ oscillators jump simultaneously (to one of the next states), while the rest remain in the same state,

$$M_r^0 = [-\Delta\xi_r(N/2)^{1/2}]^p U_r^0 \tag{30}$$

where N is the geometrical mean of the p numbers N_s and

$$U_r^0 = \int \cdots \int U^0 \chi_0 \chi_r d\tau_1 \cdots d\tau_n.$$

We shall now briefly examine the second part of M_r, corresponding to U''' (23a)

$$M_r''' = \sum_{klm} \int \cdots \int A_{klm} \chi_r \chi_0^* d\tau_1 \cdots d\tau_n \phi^r{}_{klm} \Pi'{}_{klm} \tag{31}$$

where $\phi^r{}_{klm}$ denotes the integral with respect to the coordinates ξ_k, ξ_l, ξ_m containing their product as a factor. This integral is a product of three simple ones with respect to the separate coordinates if the latter are all different, or of two simple ones if $k = l \neq m$; if $k = l = m$, it reduces to an integral with respect to one variable ξ_k containing its cube as a factor. $\Pi'{}_{klm}$ denotes the product of factors (29) for all the other normal coordinates ξ. ϕ_{klm} is different from zero in that case only if the corresponding oscillators make together three elementary jumps ($|N_{rk} + N_{rl} + N_{rm} - N_{0k} - N_{0l} - N_{rm}| = 3$), one jump each if they are all different, or a double jump and a simple one if $k = l \neq m$, or a single triple-jump if $k = l = m$.

If the total number of jumps performed by all the oscillators in the transition considered is to be equal to p, then in the product $\Pi'{}_{klm}$ only $p-3$ factors of the type (29a) must appear, so that M_r''' may be written in the form

$$M_r''' = \sum_{klm} \overset{r}{A}_{klm} \overset{r}{\phi}_{klm} [-\Delta\xi_r(N/2)^{1/2}]^{p-3} \tag{31a}$$

$A^r{}_{klm}$ being the matrix element of A_{klm} $(1, 2, \cdots n)$ with respect to χ_0 and χ_r. One can say that in the product $\phi^r{}_{klm} \Pi'{}_{klm}$ the first factor refers to jumps which are due to the direct coupling between three or two oscillators (or their anharmonicity) and the second one to the indirect coupling provided by the dependence of the vibrations on the excitation state.

The coefficients A_{klm} can be obviously defined by the formula

$$A_{klm} = \sum_{\alpha\beta\alpha} \left(\frac{\partial^3 U}{\partial x_\alpha \partial x_\beta \partial x_\gamma} \right)_0 \frac{\partial x_\alpha}{\partial \xi_k} \frac{\partial x_\beta}{\partial \xi_m} \frac{\partial x_\gamma}{\partial \xi_n}$$

where $x_\alpha, x_\beta, x_\gamma$ denote the x, y, z coordinates of the atoms ($\alpha, \beta, \gamma = 1, 2 \cdots 3n$), and the differential coefficients $\partial x_\alpha / \partial \xi_k$, etc., are the transformation coefficients which in the unidimensional case considered above were denoted by c_{kl}, equation (17). Since these coefficients are of the order of magnitude of $1/n^{1/2}$, we see that M_r''', so far as its dependence upon n is concerned, is of the order of magnitude $(1/n^{1/2})^3(1/n^{1/2})^{p-3} = (1/n^{1/2})^p$, that is, of the same order of magnitude as $M_r{}^0$ given by (30).

Now $M_r{}^0$ contains as factor the matrix element $U_r{}^0$ of the mutual potential energy of all the atoms in their normal equilibrium positions with respect to the functions χ_0 and χ_r, and this factor can be easily shown practically to vanish for all excited substates r with the exception of the one $r_1 = r_2 = r_3 = 0$ for which χ_r is symmetrical with respect to the inner coordinates $1, 2 \cdots n$ of all the atoms, that is representing an excitation wave of infinite length (having the same phase throughout the whole crystal). In fact using the expressions (8) for $\chi_r = \chi_{r_1 r_2 r_3}$ and (22a) for $\chi_0 = \phi_0$, we have

$$U_r{}^0 = \sum_{k_1 k_2 k_3} c_{rk} \int \cdots \int U^0 \phi_0{}^* \phi_k d\tau_1 \cdots d\tau_n$$

where $\phi_0 = \psi_I(1)\psi_I(2) \cdots \psi_I(n)$, and ϕ_k is obtained from ϕ_0 by replacing the factor $\psi_I(k)$ by $\psi_{II}(k)$. Introducing here the expression (3) for $U = U^0$ we get $\int \cdots \int U^0 \phi_0{}^* \phi_k d\tau_1 \cdots d\tau_n =$ sum of integrals of the type

$$\int\int U(k, l; R_{kl}) \psi_{\rm I}{}^*(k) \psi_{\rm II}(k) \psi_{\rm I}{}^*(l) \psi_{\rm I}(l) d\tau_k d\tau_l$$

with respect to all values of l. Now this sum must obviously be practically independent of k, that is of the location of the atom k within the crystal—so far as *surface effects can be neglected.* Thus the preceding expression for $U_r{}^0$ reduces to the product of a constant by the sum $\Sigma_k c_{rk}$ which vanishes (practically, again neglecting surface effects) unless $r_1 = r_2 = r_3 = 0$.

It seems questionable whether the excited substate $r_1 = r_2 = r_3 = 0$ has actually to be taken into account or not. But even if we do not exclude it, we see that the probability of a transition from this state to the normal one, so far as it is determined by $U_r{}^0$ need not be much larger than that determined by U_r''' for similar transitions from all the other excited substates, that is transitions involving the same number p of heat oscillators or rather of elementary jumps. The matrix component M_r for such transitions having the order of magnitude $(1/n^{1/2})^p$ the corresponding probability will be proportional to $(1/n)^p$. The coefficient of proportionality cannot be determined accurately unless we restrict ourselves to transitions from the substate $r_1 = r_2 = r_3 = 0$ and neglect U''' with respect to U^0. In this rather fictitious case (which it will however be well to consider for the sake of illustrating that part of the theory which is connected with the dependence of the resulting total probability upon the number of atoms n), the probability of a transition involving the cooperation of p heat oscillators, or rather *the square of the corresponding matrix element*, is given, according to (30) and (18), by

$$M_r^2 = |U_r^0|^2 \mu_r^p \tag{32}$$

where

$$\mu_r = \frac{\alpha(\Delta L_r)^2}{8} \frac{N}{n} \tag{32a}$$

L_r being an abbreviation for the product $\Delta\delta_r n$, and α being defined by (19a). α is the reciprocal of the square of a distance which depends upon the frequency ν_s of the corresponding oscillator. For oscillators of the maximum frequency in the acoustical spectrum $\nu_0 \cong 10^{13}$ this distance $1/\alpha^{1/2}$ is equal to $3 \times 10^{-9}/m_H^{1/2}$ cm where m_H is the atomic weight of the crystalline element we are considering with respect to hydrogen. We thus see that the product $\alpha(\Delta L_r)^2$ must be of the order of magnitude 1, at least for the higher frequency oscillators. For oscillators of lower frequencies it must however be smaller, so that these oscillators must be less effective in the transformation of the excitation energy into heat energy not only because their share is smaller, but because they have a smaller probability of getting this share.

In (32a) α and N denote certain (geometrical) mean values for all the p oscillators participating in the transition. Denoting the value of α for oscillators of the highest frequency with α_0, we can put

$$\mu_r = \frac{\alpha_0(\Delta L_r)^2}{8n}\left(\prod_p \frac{\nu_s}{\nu_0} N_s\right)^{1/p} \tag{32b}$$

where $\prod_p$ denotes the product over all the p oscillators we are considering.

6. THE RESULTING (STATISTICAL) VALUE OF THE PROBABILITY OF RADIATIONLESS TRANSITIONS

The minimum value of $p = p_0$ is obtained if only oscillators of the highest frequency or next to it are taken into account. This minimum value is given by

$$p_0 = \frac{E_0 - E_r}{h\nu_0} = \frac{W_{\mathrm{II}} - W_{\mathrm{I}} + W_r' - W_0'}{h\nu_0} \tag{33}$$

according to (26), and as was mentioned above is of the order of magnitude of 100. Now these oscillators can be picked up from a much larger number Q of oscillators whose frequencies are enclosed within an interval $\nu_0 - \nu = D\nu$ which can be extremely small with respect to ν but at the same time large enough to make Q exceedingly large compared with p. Limiting ourselves to longitudinal waves (which for the same wave-length possess a higher frequency than the transverse ones), we have

$$Q = \frac{4\pi v}{u^3} \nu_0^2 D\nu$$

where v is the volume of the crystal and u the velocity of the longtitudinal waves, or since $v = n\delta^3$ and $(u/\nu_0)^3 = \lambda_0^3 = 4\pi\delta^3/3$

$$Q = 3nD\nu/\nu_0. \tag{33a}$$

It must be emphasized that for a given value of $D\nu$ (or $D\nu/\nu_0$) *Q is proportional to the total number of atoms forming the crystal.* Taking $n \cong 10^{21}$ (which corresponds to a crystal with a volume about 1 cm^3) and $D\nu/\nu_0 = 10^{-13}$, say, we get $Q = 3\times 10^8$ which is still a million times larger than p_0.

Our p_0 oscillators can be picked up from the set containing Q of them *in a number of different ways,* this number being equal to

$$\binom{Q}{p_0} = \frac{Q(Q-1)\cdots(Q-p_0+1)}{1\cdot 2\cdots p_0} \cong \frac{Q^{p_0}}{p_0!}$$

that is according to (33a) proportional to the p_0-th power of the total number of atoms n.

The total probability of a transition of the crystal from the excited state to the normal one, in which the excitation energy will be shared by *any* p_0 of the Q high frequency oscillators will thus be proportional to the product

$$M_r^2\binom{Q}{p_0} = |\,U_r^0\,|^2\frac{(\mu_r Q)^{p_0}}{p_0!} = \frac{|\,U_r^0\,|^2}{p_0!}\left(\frac{3}{8}\alpha(\Delta L_r)^2 N\frac{D\nu}{\nu_0}\right)^{p_0} \tag{34}$$

that is, will be *independent of n.*

The fact that it turns out to be dependent upon the choice of the interval $D\nu$ is naturally explained by our having restricted ourselves to this interval. We can obtain some approximation to the value of the probability of any transition from the excited state to the normal one, or rather to the total value of ΣM_r^2 determining this probability by taking, in the above formula $D\nu/\nu_0 \cong 1/2$ and replacing p_0 by a somewhat larger number $p = 2p_0$ say.

The problem of the determination of the resulting transition probability P_r can be solved exactly by a method which we are presently going to describe. It must be remarked however that in deriving this probability we must not restrict ourselves to the consideration of such transitions only, for which *all* the participating oscillators jump to a higher level. On the contrary we must take account of such transitions (which are under some circumstances by far the more frequent) in which some of the oscillators jump to a higher level and others to the lower one, adding, so to say, their energy to the excitation energy.

Further it must be remembered that the "resonance condition" expressed by the equation (26) or

$$E_0 - E_r = W_{\mathrm{II}} - W_{\mathrm{I}} + W_r' - W_0'$$

need not be *exactly* satisfied. In fact we have to consider, theoretically, transitions for which the difference $E_0 - E_r$ has any value whatsoever. Let us denote the sum ΣM_r^2 for all transitions for which the value of $E_0 - E_r$ is enclosed between E and $E + dE$ by $S(E)dE$. Then the transition probability which is actually observed referred to unit time is given by [18]

$$P_r = \frac{4\pi^2}{h}S(E) \tag{35}$$

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[18] See, for instance, J. Frenkel, Einführung in die Wellenmechanik p. 211,formula (72a).

E being the resonance value of $E_0 - E_r$, that is, the excitation energy of the crystal, defined by the right hand side of equation (26). $E_0 - E_r$ can be expressed as the sum $\Sigma p_s \epsilon_s$ over all the $3n$ oscillators, where $\epsilon_s = h\nu_s$ are the corresponding energy quanta and $p_s = 0$, $+1$, or -1 for an oscillator not partaking in the transition, jumping to the next higher level, and the next lower level respectively. The total number of oscillators participating in the transition p is thus equal to $\Sigma\, |p_s|$, and the excess of oscillators gaining energy over those loosing it Σp_s. It must be remarked that for low temperatures, and in the case of the high frequency oscillators even for room temperatures jumps of the second kind (down) may not be possible, the corresponding oscillators being in the lowest state ($N_{rs} = 0$)

We shall first neglect these downward transitions, that is, restrict ourselves to the non-negative values of p_s (0, 1). We shall further, for the sake of simplicity, take the same value of μ_r given by (32a) for all the oscillators (see below).

Our problem then reduces to the determination of the value of the sum

$$\sum{}' \mu_r{}^p = S(\epsilon)d\epsilon / \left| U_r{}^0 \right|^2$$

for all values of the $p_s (=0, 1)$ satisfying the condition

$$E \leqq \sum p_s \epsilon_s \leqq E + dE \tag{36}$$

p being equal to the sum Σp_i. This problem is quite similar to the familiar problem met with in the Pauli-Fermi statistics of a gas with a given total energy E the p_s representing the possible numbers of particles in the s-th state. From the physical point of view they differ by the fact that instead of calculating the *number of states* of the whole system, that is the sum $\Sigma 1$ under the restriction (36) (the logarithm of $\Sigma 1$ being defined as the entropy), we have to calculate the sum $\Sigma \mu_r{}^p$, and further by the fact that E does not actually represent the energy of the system of oscillators but the change of this energy, the *states* thus being replaced by the *transitions*.

The restriction (36) can be removed by considering instead of the sum $\Sigma' \mu_r{}^p$ the sum $\Sigma \mu_r{}^p e^{-\beta E}$ with suitably adjusted parameter β (corresponding to the reciprocal of the temperature), extended over all possible values of the p_s. The second (unrestricted) sum is of course different from the first (restricted) one, but there exists a simple approximate relation between them. Writing the unrestricted sum in the form

$$\sum \mu_r{}^p e^{-\beta E} = \int_0^\infty S(E) e^{-\beta E} dE$$

(the factor $1/\left| U_r{}^0 \right|^2$ is dropped for the sake of brevity), we see that the integrand $S(E)e^{-\beta E}$ must have a maximum for some value of E, which by a suitable choice of $\beta (>0)$ can be made to coincide with the given value E_m lying in the interval (36). If this maximum is sharp enough, which is actually the case when E_m is not too small, we can replace the function $S(E)e^{-\beta E}$ by a Gaussian function

$$S(E_m) e^{-\beta E_m} e^{-(E-E_m)^2/\gamma^2}$$

where the parameter γ measures the width (or sharpness) of the maximum.

This gives

$$\sum \mu_r{}^p e^{-\beta E} = S(E_m) e^{-\beta E_m} \int_{-\infty}^{+\infty} e^{-(E-E_m)^2/\gamma^2} d(E - E_m) = S(E_m) e^{-\beta E_m} \gamma \pi^{1/2}$$

or

$$S(E_m) = \frac{e^{\beta E_m}}{\gamma \pi^{1/2}} \sum \mu_r{}^p e^{-\beta E} \tag{37}$$

where the (unrestricted) summation on the right hand side has to be carried out exactly.

The specified value of the parameter β can be easily determined from the condition that the "average" value E for the curve $S(E)e^{-\beta E}$ practically coincides with the extremal value E_m. This gives

$$\overline{E} = \frac{\int ES(E)e^{-\beta E} dE}{\int S(E)e^{-\beta E} dE} = -\frac{\partial}{\partial \beta} \log \int S(E) e^{-\beta} \, dE = E_m$$

or

$$E_m = -\partial \log Z / \partial \beta \tag{37a}$$

where

$$Z = \sum \mu_r{}^p e^{-\beta E} \tag{37\textit{b}}$$

is the analogue of the "state-sum" (Zustandssumme) of the usual statistical theory. The determination of the parameter γ requires some approximate knowledge of the function $S(E)$ and can be effected after the evaluation of $S(E_m)$ according to (37).

We have

$$\begin{aligned} Z &= \sum_{p_1, p_2 \cdots} \mu^{(p_1 + p_2 + \cdots)} e^{-\beta(p_1 \epsilon_1 + p_2 \epsilon_2 + \cdots)} = \prod_s \sum_{ps} \mu_r{}^{p_s} e^{-\beta p_s \epsilon_s} \\ &= \prod_s (1 + \mu_r e^{-\beta \epsilon_s}) \end{aligned}$$

whence

$$\log Z = \sum_s \log (1 + \mu_r e^{-\beta \epsilon_s}) = \int_0^{\epsilon_0} \log (1 + \mu_r e^{-\beta \epsilon}) g(\epsilon) d\epsilon \tag{38}$$

$g(\epsilon)d\epsilon$ being the number of oscillators whose energy quanta $\epsilon = h\nu$ lie between ϵ and $\epsilon + d\epsilon$. Restricting ourselves to longitudinal waves we have

$$g(\epsilon) d\epsilon = 3n\epsilon^2 d\epsilon / \epsilon_0{}^3 .$$

Now μ_r being a very small number (of the order of $1/n$) we can put with sufficient accuracy

$$\log(1 + \mu_r e^{-\beta\epsilon}) = \mu_r e^{-\beta\epsilon}$$

which gives

$$\log Z = \frac{3n\mu_r}{\epsilon_0{}^3}\int_0^{\epsilon_0} e^{-\beta\epsilon}\epsilon^2 d\epsilon. \tag{38a}$$

This formula shows at once that Z *is actually independent of* n; the same follows from (37) and (37a) for β and for $S(E_m)$, the quantity which determines the probability for which we are looking.

The above results can be easily generalized to allow for the difference of the factor μ_r for different oscillators. Replacing $\mu_r{}^p$ by the product $\Pi\mu_{rs}{}^{p_s}$ we get formulae of the same type as before. In evaluating log Z according to (38) or (38a) we have to consider μ_r as a function of the index s or of the energy $\epsilon(=\epsilon_s)$.

Denoting the value of μ_{rs} for $\epsilon=\epsilon_0$ and $N_s=1$ with μ_r we have

$$\mu_{rs} = \mu_r\epsilon_s N_s/\epsilon_0$$

so that instead of (38a) we get

$$\log Z = \frac{3n\mu_r}{\epsilon_0{}^4}\int_0^{\epsilon_0} e^{-\beta\epsilon}\epsilon^3 N(\epsilon) d\epsilon. \tag{39}$$

The average value of $N(\epsilon)$ at the temperature T under the assumption of statistical equilibrium is given by Planck's law $N(\epsilon)=1/(e^{\epsilon/kT}-1)$. If we assume this distribution to hold for the initial (excited) state of the crystal then (since $N_{rs}=N_{0s}-1$) the preceding expression has to be increased by 1, the average value of $N(\epsilon)$ thus being

$$N(\epsilon) = 1/(e^{\epsilon/kT} - 1) + 1 = 1/(1 - e^{-\epsilon/kT}). \tag{39a}$$

The above theory can be applied to the estimation of the probability of transitions of the opposite character, that is from the normal state to the excited one, so far as all the participating oscillators jump in the same sense, that is downwards, their energy being converted into the excitation energy. In this case we have to put of course

$$N(\epsilon) = 1/(e^{\epsilon/kT} - 1). \tag{39b}$$

It can be easily shown that our simplified theory, which takes into account jumps of the same sense only, holds for the limiting case that the product $n\mu_r$ (which is independent of n and which is a measure of the change of atomic distance produced by excitation) is very small. The probability of transitions in which p oscillators take part being approximately proportional to $(\mu n)^p/p!$ (cf. equation (34)) a strict economy in the use of the different oscillators will be observed in this case, their number being reduced to the minimum $p_0=(E_0-E_r)/h\nu_0=E_m/\epsilon_0$ and "useless" jumps in the wrong sense practically excluded.

To get a rough idea of what will take place in the opposite case, that is if μn is large, we have to sum up the preceding expression for all values of p starting with $p = p_0$. If $\mu n \ll p_0$ this sum will still practically reduce to the first term. If however $\mu n \gg p_0$ it can be replaced by the sum $\sum_{p=1}^{\infty} (\mu n)^p / p!$ giving $e^{\mu n}$. The same result is obtained by replacing the sum by its maximum term, which corresponds to $p = \mu n$ and putting $p! = (p/e)^p$.

The method applied above for the approximate evaluation of the restricted sum of the products $\mu_{rs} |^{p_s}|$ is no longer applicable when the numbers p_s are allowed to take negative values (-1), for the simple reason that the function $S(E)$ has no tendency to increase in this case with increase of E. To the contrary it has a very flat maximum for $E = 0$ and vanishes for $|E| > \Sigma \epsilon_s$. One could get rid of this restriction $E < \Sigma p_s \epsilon_s < E + dE$ in this case by a more general method, involving the use of Dirichlet's disruptive multiplier.[19] It does not seem worth while however to develop this method at a greater length here and we shall satisfy ourselves by making a direct calculation for the simplified case $\epsilon_s = \epsilon = \text{const}$. Our problem can then be stated as follows: The number n is expressed as the sum of three numbers $n' + n'' + n'''$, denoting respectively the number of positive, negative and zero values in the sequence $p_1, p_2 \cdots p_n$; to determine the sum $\Sigma' \mu^{n'+n''}$ under the restriction that $n' - n'' = p_0 = E/\epsilon$.

Since each "partitio" $n = n' + n'' + n'''$ can be effected in $n!/n'!n''!n'''!$ different ways (by permuting the numbers p_i) we get

$$\sum{}' \mu^{n'+n''} = \sum_{n''=0}^{n-p} \frac{n!}{n'!n''!n'''!} \mu^{n'+n''} (n' = n'' + p_0,\ n''' = n - 2n'' - p_0).$$

The ratio of the n''-th term of this sum to the preceding one is equal to

$$(n - 2n'' + p_0 + 1)(n - 2n'' + p_0 + 2)\mu^2 / n''(n'' + p_0)$$

or approximately so long as n'' is small compared with n

$$(n\mu)^2 / n''(n'' + p_0).$$

The maximum term is that for which this ratio is equal to 1, the condition $n'' \ll n$ being obviously satisfied for $n''(n'' + p_0) = (n\mu)^2$. Replacing the sum by its maximum term we have

$$\sum{}' \mu^{n'+n''} \cong (n\mu)^{n'+n''} / n'!n''!$$

This gives if $n'' \gg 1$ using Stirling's formula

$$\sum{}' \mu^{n'+n''} = \frac{(n\mu e)^{2n''+p_0-1}}{2\pi n''^{n''} (n'' + p_0)^{n''+p_0}} \tag{40}$$

where

$$n'' = [(n\mu)^2 + (p_0/2)^2]^{1/2} - p_0/2. \tag{40a}$$

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[19] That is the integral $\int_0^\infty sn\, ax \cos bx\, dx/x$ which is equal to $\pi/2$ for $a > b$, $-\pi/2$ for $a < b$ and $\pi/4$ for $a = b$.

If $n\mu$ is much larger than p_0 we can put $n''=n\mu$ and reduce the above sum to

$$\sum{}'\mu^{n'+n''} \cong e^{2n\mu+p_0}/2\pi n\mu.$$

In the opposite case ($n\mu \ll p_0$) we have $n''\cong(n\mu)^2/p_0$, the result given by (40) being practically the same as in the case $n''=0$ which corresponds to one-sided jumps, that is

$$\sum{}'\mu^{n'+n''} \cong (n\mu)^{p_0}/p_0!$$

Which case is usually met with in practice, is difficult to say.

7. RADIATIVE TRANSITIONS (ABSORPTION AND EMISSION OF LIGHT)

We have considered heretofore only radiationless transitions of the crystal from the excited state to the normal one or vice versa. We must now briefly examine such transitions which are connected with the absorption or emission of light. As has been pointed out in the introduction the excitation of a crystal by incident radiation forms the first stage of the process of light absorption, the second stage being provided by the radiationless transition to the normal state.

The energy levels or spectral terms which have to be considered in this connection are those that have been discussed already in the preceding sections, the energy of one of the excited sub states with respect to the normal state being given by (26). Since there are n-substates, corresponding to one single excitation state of an isolated atom, there must appear in the spectrum of a solid body in general n lines, corresponding to one single line in the spectrum of the gas, so far of course as the initial or the final state is the normal one. The frequencies of these lines, which can be described as forming an "excitation multiplet" are given by

$$\nu_r = (1/h)(W_{\mathrm{II}} - W_{\mathrm{I}} - W_0') + W_r'/h \tag{41}$$

if vibrational transitions are not taken into account. Allowing for these transitions we get a still larger number of spectral lines with frequencies differing from the preceding ones by the amounts

$$\Delta\nu_r = \sum\left[\nu_{rs}(N_{rs} + \tfrac{1}{2}) - \nu_{0s}(N_{0s} + \tfrac{1}{2})\right]. \tag{41a}$$

The spacing between the main lines (41) is determined approximately by the expression (15) or (8a). It is the smaller, the larger the number of atoms in the crystal. The total width of the multiplet formed by all these lines, is however independent of n and equal approximately to V_0+6V_1, where

$$V_0 = \int\int U(k, l)\,|\,\psi_{\mathrm{II}}(k)\,|^2\,|\,\psi_{\mathrm{I}}(l)\,|^2 d\tau_k d\tau_l \tag{42}$$

and (for the case of a simple cubical lattice)

$$V_1 = 6\int\int U(k,l)\psi_{\mathrm{II}}^*(k)\psi_{\mathrm{I}}(k)\psi_{\mathrm{I}}^*(l)\psi_{\mathrm{II}}(l)d\tau_k d\tau_l \tag{42a}$$

k and l denoting two neighboring atoms. This width is of the same order of magnitude, or perhaps just a few times larger, than the shift in the spectral levels of two atoms, produced by their combining together into one molecule. The maximum spacing between the lines of such a multiplet is of the order of $2V_1/n$, that is, so small that they should appear in practice as a continuous band even if they had no satellites due to the accompanying vibrational jumps and no natural width, which is measured by the probability of radiationless transitions we have examined before. This natural width (equal to the "mean life" of the corresponding excited substate), being independent of n must be much larger than the spacing between the consecutive lines. We thus see that the resolution of the continuous (band) spectrum of a solid body into single lines, which has been observed by J. Becguerel in the spectra of some rare earths at the temperature of liquid air and recently by W. Obreimow[20] in iodine and other substances at very low temperatures (of liquid hydrogen or helium) cannot be explained without special assumptions about the separation of the lines of an excitation multiplet or their intensities.

It can occur, namely, that for some excitation state II the "exchange energy" (42a) is abnormally small, so that the whole multiplet will appear as a single line, accompanied by satellites due to the vibration jumps. Since the coupling of the electronic states with the vibrational ones is determined partially by the same energy V_1, as the width of the excitation multiplet (see for instance formula (15a) for the change of the crystal lattice δ), these satellites will be rather faint. This may account for the lines observed by Becquerel, which were not very much influenced by the temperature.

Another possible explanation is that only a few of the excited sub-levels can combine with the normal one, these combinations forming a series of more or less widely spaced lines. Now the natural width of these lines due to radiationless transitions will be the smaller the lower the temperature, for as we have seen the coefficients μ_{rs} which determine the probability of such transitions are proportional to the average values of the quantum numbers N_s and must therefore decrease as the temperature decreases. At the same time and in the same measure will the intensity of the satellites decrease due to vibrational jumps. It can thus happen that for sufficiently low temperatures the continuous spectrum of the solid body will be resolved into separate lines, in accordance with Obreimow's observations.

It is however hardly possible to substantiate the above explanation by actual calculation of the intensities of spectral lines, that is of the probabilities of transitions connected with absorption or emission of radiation.

In the simple case of an atom or a molecule these probabilities are determined by the matrix elements of the resulting electric moment of the system. In the case of a molecule consisting of n identical atoms this sum is a symmetrical function of their electronic coordinates $1, 2, \cdots n$. Replacing the molecule by a crystal and considering pure electronic transitions not accompanied by vibrational jumps, we get for the matrix element of this

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[20] W. Obreimow and Proc. Amsterdam Acad. de Kaas 31–3, p. 353 (1928).

symmetrical function $P(1, 2, \cdots n)$ with respect to the functions χ_r and χ_0 a value which can be shown to be zero for all the excited substates with the exception of the symmetrical one (by the same argument as in Section 5). It thus seems that, as a matter of fact, the whole multiplet will be reduced to one single line, or there will be no lines whatever if the symmetrical excitation state cannot be realized.

This argument is however fallacious, for in the case of a crystal whose linear dimensions are large or even comparable with the wave-length of the absorbed or emitted light the probability of absorption or emission will be determined not by the resultant electric moment $P(1, 2, \cdots n)$ but by a sum of the moments of the separate atoms $P_k(k)$ multiplied with *certain phase factors, which depend upon the positions of these atoms* R_k. In case of a system of plane electromagnetic waves (of resonance frequency) propagated within the crystals in the direction x, say, with the phase velocity w, these factors would be $e^{i2\pi\nu x_k/w}$, so that the probability of absorption of a single light quantum, that is of the excitation of a single atom, would be measured by the matrix elements with respect to the functions χ_r and χ_0 of the sum $\Sigma P_0(k)e^{i2\pi\nu x_k/w}$. There is no reason why these matrix elements should vanish for most of the substates r, remaining different from zero for a few others.

The computation of the excitation probabilities by the above method can hardly give perfectly correct results, a more consequent quantum-mechanical treatment being necessary in order to obtain them, but it seems fairly certain on the basis of these crude considerations, that nothing like a selection rule for the different terms of an excitation multiplet can be expected to exist.

It is possible that the phenomenon observed by Obreimow is limited to the case of compound substances, which lie outside the scope of this investigation. Preliminary results which I have obtained for such compound crystals, seem to support this conclusion.