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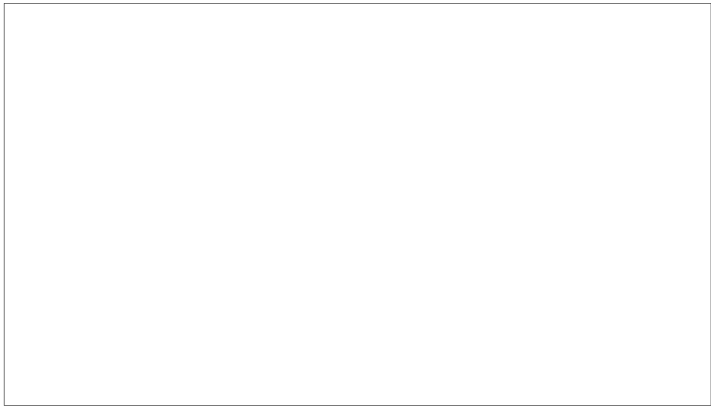
THE TRANSFORMATION OF ENERGY IN SOLIDS

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THE TRANSFORMATION OF ENERGY IN SOLIDS

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The electron gas of a crystal and the crystal lattice are coupled with each other as regards energy. Hence, energy can be taken up from the electron gas by the lattice and vice versa. Apart from the simple collisions between electrons and the lattice, observed by BLOCH, there are, especially at high temperatures, processes (multiple collisions) in which the amount of transferred energy is very great. The temperature dependence of the effective cross section is shown. Finally it is shown how very fast electrons inside the crystal place themselves in thermal equilibrium with the electron gas. Calculations are made to find the time required to reach this equilibrium.

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When considering the forms of energy of a solid, we are accustomed to make a sub-division into two parts: the energy of the lattice and the energy of the electron gas. Naturally these two are not independent of each other. The conditions are similar to the case of molecules, where the energy of nuclear oscillation, or rotation, and of electrons can be separated from each other. These three forms of energy, also, are not without interaction amongst each other: the rotation, through centrifugal force, influences the binding-force of the molecule, the amplitude of nuclear oscillation affects the moment of inertia and finally, the electron jump is a decisive factor in the binding strength of the molecule and it is known that a dissociation of the molecule can be brought about by the excitation of higher electron jumps.

In the case of solids also it will have to be assumed that the excitation of higher electron energies will cause a change in the lattice stability. Nevertheless, in every case resulting from the radiation of visible and ultraviolet light of not too small wave length, it is probable that the variation in lattice stability may be neglected: obviously there is no strong coupling of the two forms of energy of solids. For this reason we think that the following considerations can be regarded as valid, for instance for the excitation of the electron into the first band above the ground state.

There is, moreover, an analogy here to diatomic molecules, in the case where for the excited and unexcited state the two potential curves are nearly identical, the minima lie one over the other, etc. Therefore, it is clear, from the Franck-Condon principle, that to a first approximation no conversion of electron energy into energy of nuclear oscillation can take place. We consider the corresponding assumption to be all the more justified since the elevation of one or several electrons from the lower to the upper band represents an incomparably smaller interference with the bonding stability of the solid than is the excitation of a molecule-electron, since the number of the electrons constituting the cohesion of the solid is very great. We consider ourselves entitled,

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therefore, to neglect the considerations of v. HIPPEL (1) *
for our purposes.

At this point we must discuss the objections which have been raised
recently against the rigid application of the band model of the solid.
More especially we would refer to the works of **FRENKEL** (2) and **SLATER**
(3) who have called the band model "sophisticated". Thus, Slater holds
that a theory of solids must reproduce the following three energy states,
which result from the quite primitive conception of a solid as a
conglomerate of single atoms or molecules: 1. Excitation of the electron
into a state in which the electron possesses a certain energy above the
ground state, without being free, but where this condition may be transferred
from one atom to any neighbouring atom (Frenkel excitons); 2. Complete
ionisation, the electron becoming freely mobile; 3. Ionisation with
immediate recombination or addition to neighbouring atoms.

A criticism of the band model is that it makes no allowance for
distinction between these three types of behaviour. An excited electron
is practically always freely mobile and has no possibility of recombination
or addition which can be localised. We cannot support this criticism of
the band model because, for example, the objection that the electrons in
the conduction band must always exhibit an infinitely great conductivity
disappears at once on taking into account the interaction with the
lattice. Neither do we quite see to what extent consideration of the
Coulomb force between electron and ion is supposed to give a better
approximation, because this is already included in a first approximation;
the periodic potential of course depends above all on the ions of the
lattice and it would be superfluous to take this into account a second time.

Moreover, in our view, the formation of solid and liquid substances,
and also of molecules, is pre-eminently connected with the existence of
non-coulomb electron forces, viz. the chemical linkage forces which give
rise to a very intimate fusion of the individual atoms. It is not
surprising, therefore, that these structures exhibit properties widely
divergent from those of single atoms and we do not think there is any
special purpose, when describing absorption in a solid, to refer to the
behaviour of an electron with respect to one of the partners in the
combination. In those cases, however, where the actual chemical linkage
forces are not so important, as for example in molecule lattices and perhaps
also in the polymerides studied by SCHEIBE and his collaborators (4)
the Frenkel exciton idea can be profitably used.

Finally, attention must also be drawn to the fact that there is no
ground for supposing that there is any contradiction between the
experimental facts which are known today and the band model explanation
with its consequential observation of the reaction with the lattice.
It must also be remembered, of course, that the character of the crystals
is by no means perfect and that they continually exhibit the presence of
impurities and deviations from the stoichiometrically correct state.
The importance of these facts, especially the strong influence exerted by
impurities, internal stresses, loose spots, and similar conditions, on the
electron spectrum of the crystals, has been discussed systematically by
SMEKAL (5). There seems to be not the slightest doubt that a development
of the band model in this direction is both necessary and profitable.
Even though in this work we do not digress from the case of the ideal
crystal, yet we shall frequently indicate the necessity for generalisations
of this kind. Besides this, from the theoretical point of view, we have

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* See references at end

devoted two special papers to the application of the present conceptions
to actual crystals. (6).

LATTICE ENERGY

We think of the lattice as approximately harmonic, i.e. the lattice
energy may be represented as the quadratic form of the elongations of the
atoms from their positions of rest.   In these circumstances, as Frenkel
stated, and as is also the basis for the original ideas of Debye, the
energy spectrum of a solid can be treated as an analogy to the light quanta
gas of cavity radiation.   We shall speak, therefore, of sound quanta of
a definite frequency ν, the energy being h. ν and the impulse

$$h : \lambda \left(\lambda \text{ wavelength} \right).$$

The only difference from cavity radiation is that a limiting frequency
exists;   it is given by the quotient: speed of sound divided by the
lattice constant, and hence is of the order of 10^{13}. *

The sound quanta fulfil the Bose statistics and their spectral
energy distribution follows Planck's law.   We shall further show that
the sound quanta, similarly to light quanta, give "reaction equations" of
trinomial form (7).

ELECTRON ENERGY

According to the Kronig conception, the spectrum of electrons in a
solid can be represented by bands, separated from each other by forbidden
zones, of which the uppermost band containing electrons may be fully
occupied - as in insulators - or partially occupied - as in metallic
conductors.   We shall only make passing references here to special cases
which may arise through the presence of deviations from the regular
structure or from foreign atoms in the lattice (8) and which lead to semi-
conductors (9) or crystal-phosphors (10).

The electron energy is distributed over all the electrons in conformity
with Fermi statistics;   if in one band there is only a small number of
electrons (small in relation to the number of terms of the band), the
Fermi distribution can be approxi ted, as is known, from the Maxwell
distribution, i.e. the electron gas can be regarded as free in the
classical sense (11)

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*   This distinction is not essential since equally
large frequencies can be introduced when
considering electromagnet radiation.   As an
example $C : r_o$ where r_o is the fundamental
wavelength.

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ABSORPTION BY THE LATTICE

It is a known fact that a harmonic oscillator can absorb electro-magnetic energy, if it has a dipole moment different from zero *
Here, the selection rules permit only the simultaneous absorption of one natural oscillation quantum per oscillator, i.e. an amount only relatively little above the thermal energy level, since as a general rule, at about room temperature a very large number of lattice quanta has already been excited.

The optical absorption of the lattice can be observed in the long-wave infra-red (5 to 15µ) and is generally present only in the case of ionic crystals because it is only in this case that a branch of the oscillation spectrum of atoms with a **non-disappearing dipole moment** exists. In the interaction between the electrons and the lattice, however, it is not only the "optical branch" of atomic oscillations which is operative, but also the so-called "acoustic branch" which only appears in homogeneous solids, as for example the diamond. For our purposes, therefore, there is no point in making a distinction between the acoustic and the optical branch of the atomic oscillation spectrum and this will not be done. When there is a reference to the spectrum of the elastic vibrations of the lattice, both branches, so far as they are present, will be intended.

In the case of non-ionic crystals, no optical absorption is observed in the long-wave infra-red. Further, there is no absorption in the short-wave infra-red in the case of insulators (12). This is in contrast to metals where the absorption is caused by electrons.

ABSORPTION BY THE ELECTRONS

The electrons in a solid body can absorb electromagnetic radiation. Investigations of solid substances show that the creation of excited electron states by the absorption of radiation can take place in various ways:

According to the classic theory of metals, the electromagnetic wave produces an acceleration of the free conduction electrons. These give up their excitation energy to the lattice in the form of heat, i.e. by collision with the ions.

* In this paper the word absorption is used in the nuclear physical sense i.e. the transformation of radiant energy into some other form of energy such as the kinetic energy of a particle or the potential energy of an atom or electron. In contrast the word absorption in thermodynamics indicates the transformation of the absorbed radiant energy into all possible forms of energy in the sense of establishing thermal equilibrium. In the present work thermodynamic absorption would consist of a series of successive nuclear physical processes. The primary process is the absorption of energy by an electron by an amount considerably in excess of the mean thermal energy. This state would then dissipate its energy by interaction with the enviroment. (Second type collisions).

This process in itself is perfectly represented by the Drude-Riecke theory of metals.

According to the quantum theory, when evaluating the doubtful process, the method must form not only a theory of disturbance for the outer electromagnetic fields, but must simultaneously take into account the disturbance caused by thermal fluctuation of the lattice potential. We then obtain as a first approximation, the terms giving rise to optical reflection and scattering and also terms descriptive of a transition of electron energy into lattice energy (which will be explained later). As a second approximation we obtain terms representing a simultaneous process between electron energy and lattice energy. It is characteristic of the latter process that, instead of the law of conservation, applicable to the reduced propagation vector, we have the equation:

$$k' = k \pm q$$

where k is the propagation vector of the initial state, k' that of the end state and q the impulse vector of the sound quanta generated or absorbed. The probability of such a process when a sound quantum is generated is proportional to $N_\nu + 1$, and when it is absorbed, proportional to N_ν, where N_ν stands for the number of sound quanta in the frequency range ν, $\nu+d\nu$.

As a result of the changed impulse conditions, it is possible with such a process to excite optical electron terms representing transitions in the same band, while with absorption based on the quantum theory transitions to different bands only can occur, if there is no participation by the lattice.

The energy taken up by the electrons in this way can be and is given up to the lattice through interaction with the lattice (first approximation of the perturbation process). The whole process is naturally dependent upon temperature since the N_ν are temperature dependent. However, although the N_ν disappear at the absolute zero, the process described above certainly does not disappear, because, owing to the spontaneous generation of sound quanta (the summand 1 in $N_\nu + 1$), both the absorption of energy by electrons and the transmission of this to the lattice are possible even at the absolute zero. This latter process, however, presupposes that the upper-most band containing electrons is not fully occupied, because otherwise the Pauli principle forbids absorptions of this kind. Hence, these transitions are reserved exclusively to metallic conductors, which of course are characterised by half-filled bands. This finding also agrees with the experimental fact that this type of absorption has never been observed in insulators. For metals, however, the result deviates from the classic finding of "acceleration absorption" in that, according to the quantum theory, even at absolute zero there should still be a slight infra-red absorption. This should be much smaller than could be assumed from what has just been said, since, according to the Pauli principle, at absolute zero only an incomparably small number of electrons can participate in the absorption, which may therefore be regarded as practically zero. The reason for this is the same as that for the disappearance of electrical resistance at low temperatures, in spite of the existence of spontaneously generated sound quanta.

Essentially, moreover, the two processes of classic absorption and electrical conductivity are the same, because the absorption process

described here is valid for electro-magnetic fields, the oscillation of
which may be as slow as required, and hence must still hold some meaning
even for the limit case of a constant electrical field.   Here, too, the
perturbation calculation can be carried out in exactly the same way.   The
transfer of energy from the electron gas to the lattice takes place in the
same manner as before with identically the same mechanism.   From this
consideration there emerges directly the close relationship between the
absorption coefficient and conductivity asserted by classical optics.
Such a relationship is naturally no longer valid in the case of genuine
quanta absorption (band to band transfer).

Attention is drawn to the fact that reflection and scattering
according to the quantum theory can also be attributed to the (intermediate)
excitation of quantum states in the higher bands.   Since these upper bands
are quite free from electrons, both in the case of metals and of insulators,
it can be concluded that, qualitatively at any rate, both metals and
insulators must exhibit the same behaviour with regard to reflection which
depends upon this process.

It is generally possible for other transitions to occur, in the case
of atoms, which would not be permitted from a first approximation of the
solution of the perturbation equation.   This always happens when two levels.
between which the electrical transfer moment disappears, can combine with
a third level.   There is no question of this possibility, however, in the
case of electron gas.   For when two levels are combined with a third, each
of the propagation vectors of these two levels must be in conformity with
the propagation vector of the third.   It is clear that in that case the
propagation vectors of the two first states must also agree with each other.
Then, however, there is also the possibility of transfer between the two
first levels and this transfer already appears, in the first approximation
of the perturbation equation as a dipole transfer.   It is only when - to
some extent by chance - the integral over the unit cell

$$\int e^{\, i \left(k \, - \, \frac{2\pi n \nu}{c} \, \gamma - k' ; \, r \right)} u^{*}_{n'k'} \left[\frac{\partial u_{nk}}{\partial x} + i k_{x} u_{nk} \right] d V$$

(γ unit vector in the direction of propagation of radiation, n index of

refraction) disappears, **in spite of** the condition

$$k' = k \pm \frac{2\pi n \nu}{c} \cdot \gamma$$

being fulfilled, that the dispersion theory can yield new transitions at a
second approximation.

If we start from the band model of a solid it is possible, both for
metals and insulators, to have genuine optical absorption in the form of
an electron being elevated to a higher band.   In this case we speak of
an excitation of the electron, by analogy to atomic electrons.   In this
transition, the selection rules which have been discussed are applicable;
they signify the maintenance of the propagation vector.   The extent of
absorption of this kind can probably be estimated approximately by
assuming the validity of the Thomas-Kuhn sum rule and assigning the total
number of electrons capable of absorption to the total absorption of the
substance in question.   These then distribute themselves over the total
absorbed continuum, so that if the breadth of the spectral absorption is
known, the f-number per frequency interval can also be given at least
approximately.

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THE TRANSFORMATION OF THE ENERGY OF THE EXCITED ELECTRON INTO LATTICE ENERGY.

An optically excited electron, i.e. one elevated to a higher band by absorption of electro-magnetic radiation * will possess an energy here which is considerably greater than would correspond to equilibrium with the lattice. Thus, in the course of time energy must be given off and we must discuss what possibilities there are for the emission of energy from an electron in the upper band.

a) In practice a return of the electron to the lower band, with the emission of energy. The reason for this must presumably be sought in the selection rules for electron transition between the bands, which require agreement of the propagation vectors, not only in respect of size but also of direction. One exception is the so-called crystal phosphors where as has been shown by Schön (13) and Reihl (14) the return of an electron from the upper to the lower band by way of intermediate processes is possible, these processes consisting in the recombination of the electron from the upper band with a discrete term of an ion and then a kind of autoionisation of the ion in the direction of the lower band (15). In pure crystals a return of the electron to the lower band with emission of energy would only be possible if the electron were not exposed after absorption to any kind of perturbation, i.e. as we shall show later, at room temperature only within times of the order of 10^{-10} to 10^{-12} sec.

b) The interaction with the lattice may be considered in terms of both the classic and the quantum theory conception. First let us take a look at the classic conception, as a crude but qualitatively useful picture. As has already been mentioned, if the number of electrons in the upper band is small compared with the number of the terms of the upper band, the electrons can be regarded as free, to a high degree. The classic conception amounts to denying any consideration of the properties deriving from the regular construction of the lattice. In such circumstances the motion of the electrons in the ion lattice corresponds entirely to that in the plasma of a gas. Let us imagine that into such a plasma, the temperature of which amounts to about 300° absolute, an electron with 1 volt energy is introduced. This corresponds in practice to the case where radiation is absorbed which exceeds in energy the long wave limit of the fundamental lattice absorption by about 1 volt. We are concerned with the time during which the electron reaches thermal equilibrium with the lattice. To do this it has to give up much of its energy. We assume that this happens essentially through elastic impacts with the lattice. According to Cravath (16) the amount of energy f, removed from the electron at each collision with an ion is:

$$f = -\frac{8}{3} \frac{m_e M_i}{(m_e + M_i)} \left(1 - \frac{T_g}{T_{el}}\right), \quad T_{el} = \frac{mv_{el}^2}{2k}, \tag{1}$$

where m_e is the electron mass, M_i the mass of the ion, T_g the temperature of the lattice, and T_{el} the temperature of the electrons. For high electron temperature and low lattice temperature we can put:

$$f = \frac{8}{3} \frac{m_{el}}{M_i}, \tag{2}$$

* We limit ourselves in what follows to the particularly clear case of excitation by absorption; naturally these considerations apply also to the case where the electron is excited by collision with a fast moving electron. They will be valid for the case of crystal excitation by electron collision and for the electrical break down of solid and liquid insulators.

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which is of the order of 10^{-5} to 10^{-6}. Where $T_g \sim t_{el}$, f decreases, as a result of the reverse process (transfer of energy from the lattice to the electrons) until finally, with equality of temperature $f = 0$.

Apart from the magnitude f, another factor which is decisive for the rate of energy surrender is the number of collisions Z:

$$Z = \frac{l}{v} , \qquad (3)$$

where l is the mean free path, v the trajectory velocity of the electron. In our hypothetical case of the 1 volt electron, v is of the order of 10^8 cm per sec. The mean free path depends on the velocity of the electron, as can be deduced from the works of Fröhlich and Mott (17). This is due to the fact that the impact number per electron per second, as can be computed in quite a general way from the quantum theory, is always of the order 10^{13} and so, correspondingly for lower velocities, the mean free path must decrease. If, for example, we assume a mean free path of 10^{-5} for electrons of a few volts in energy, as in metals, then for crystals of insulators with sparsely occupied energy bands, where the electrons have, thermally the same temperature as the lattice, say 1/100 volt average energy, we must assume approximately the value of 10^{-7} to 10^{-8}. If we take a simple impact number 10^{13} and make allowance, according to equation (2) for the fact that about 10^5 to 10^6 impacts per second are necessary * to make the energy of the electron agree with that of the lattice, we arrive at times of 10^{-7} to 10^{-8} sec. This time is longer for slower electrons because then, owing to the appearance of the inverse processes according to equation (1) the fraction of the energy transferred at each impact becomes less.

The following comments must be made, however, in addition to what has been said already: when applying the Cravath formula, we have tacitly assumed that the ions can be regarded as free for the process of collision with the electrons, so that the laws of elastic impact are therefore valid. The equilibrium time is then the shortest obtainable under the assumption of elastic transfer of energy. In reality the ions are held together by the lattice binding forces; this linkage can be looked upon as an extension of the effective ion mass. In the limit case of a completely rigid lattice, practically no energy is absorbed from the lattice, so that an infinitely long equilibrium time would result: In practice the value will lie between the two extremes, the one considered by us and the one with the completely rigid lattice. The important factor is the binding strength of the lattice in relation to the energy of the fast electron. If the energy of the electron is very great the model of the free ions will be satisfactory, while if the energy is slight compared with the binding energy, that of the rigid lattice will be valid. There is no need to discuss these conditions in detail here because we have still to deal with the quantum theory conception.

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* This hypothesis merely states that the "Relaxation path" that is, the distance beyond which the electron passes to attain equilibrium with the lattice is greater by the stated factor than the mean free path in equation 3, which is only given by impulse variation. See in this connection R. ROMPE and M. STEENBECK, Ergebn. d. exakt. Naturw. XVIII. 1939.

c) SIMPLE IMPACTS WITH THE LATTICE.   In contrast to the classic theory there are no unqualified impacts between electrons and lattice molecules in the quantum theory.   This is an essential difference by comparison with the classic theory.   As long as the lattice components are at the stoichiometrically correct lattice points, there is no interaction with the lattice.   Not until there is heat transfer with the lattice does the situation change.   Correspondingly, the energy of interaction between the electrons of the lattice and the structural units of the lattice is of such a nature that it disappears directly if no lattice waves exist.   Bloch (18) in his theory of electrical conductivity lays down the formula

$$\ddot{V} = - (\mathbf{u}: \text{grad } V),$$

where V stands for the Coulomb potential between the electron and the structural units of the lattice and u is the value indicating the displacement of any point of the metal; it disappears when every point of the metal is in its equilibrium position.

The potential $\ddot{V}$ gives rise to a perturbation matrix $\ddot{V}_{n,m}$, by means of which the Dirac perturbation equations for the problem can be worked out:

$$\frac{h}{2\pi i} \frac{\partial c_n}{\partial t} = \sum_m \ddot{V}_{n,m} c_m .$$

The solution of this equation is performed in the usual way, a limit being made at the so-called first approximation.   This restriction neglects multiple collisions (one electron and several lattice waves).   The results of computations and comparison of these with actual experience seem to justify this omission.

Yet another simplification will be made.   For the reduced impulse vector   of the electron before the impact and its value k' after the impact, a kind of law of conservation is applicable

$$k' = k \pm q + 2\pi g .$$

where q is the propagation vector of the lattice wave and g is an integral vector, built up from the components of the reciprocal lattice. Bloch, in his theory, only takes into consideration transitions where $g = 0$, while the case $g \neq 0$ has been allowed for qualitatively by Peierls (19) as a reversal process.

In general the reversal processes take place with very little transfer of energy to the lattice, which is why they are only noticeable at very low temperatures as regards conductivity.   Thus we can regard them as the elastic reflections of the electrons at the lattice waves, the propagation vector of the electrons changing only its direction and not its magnitude. Since in these circumstances our chief interest is the surrender of energy to the lattice, we may therefore make the same simplifications as Bloch.   We cannot, however, draw any conclusions from our results concerning the times which elapse between two successive collisions of an electron with the lattice.   The reason for this is that these times are closely

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related to the processes in which there are perceptible changes of direction, but no changes in energy. It must be assumed that, in the computation of these collision times, the elastic reflections play a much greater part than the energetically effective collisions, for it appears that, when computing the collision times solely for energetically effective impacts, the order of magnitude which results is different from what could reasonably have been expected (about 10^{13} collisions per sec.).

From the Sommerfeld perturbation equation for the interaction between the electrons of a metal and the lattice vibrations we derive the following result (20)

$$\left| c(k - q; \, N_\nu + 1) \right|^2 = \frac{2C^2 q^2}{G^3 . 9 . M . h\nu} \, (N_\nu + 1) f(E_{k-q} - E_k + h\nu).$$

Here, the function f signifies

$$f(x) = 2 \, \frac{1 - \cos \frac{2\pi x t}{h}}{\left(\frac{2\pi x}{h} \right)^2}$$

the value C is essentially the kinetic energy of the electrons, an approximately known value, of the order of a few volts for the case of a metal; q is related to the speed of sound u, in the crystal,

$u = \frac{2\pi\nu}{q}$ which is approximately of the order 10^5 cm/sec, and ν is the frequency of a sound quantum ; its order of magnitude lies therefore between 0 and 10^{13}. G is a constant.

The signification of the value $\left| c(k-q; \, N_\nu + 1) \right|^2$ is as follows:

If we multiply again by dZ_ν, the number of acoustic natural oscillations in the frequency interval ν, $\nu + d\nu$, this value is a direct representation of the probability that an electron will pass from the state with the propagation vector k to the state with the propagation vector $k-q$ and that at the same time a quantum with the frequency v will appear. This probability varies with time. There is as a rule no connection at all between the energy change of the electron and the energy of the newly formed sound quantum, in accordance with the fact that, from the uncertainty relations between energy and time, the law of conservation of energy is, for a short time, not fulfilled at all. That is, there is no necessity at all for the validity of

$$E_{k-q} - E_k + h\nu = 0.$$

Other transitions, too, have a finite, though small probability. This is connected with the fact that it is only for infinitely large time values that the energy law must be fulfilled.

It is now possible to bring the function f appearing in $\left| c \right|^2$ into the form:

$$f(U) = 2t^2 \frac{1 - \cos U}{U^2}$$

where

$$U = \frac{t}{h}\left(E_{k-q} - E_k + hv_{\bar{q}}\right)$$

Thus, for large values of t, the function f has approximately the character of a δ-function: preponderance of the function value at the point $U=0$. This means, essentially: establishment of the law of energy for very large time values.

The number of acoustic natural oscillations in the interval q_1, $q_1 + dq_1$; q_2, $q_2 + dq_2$; q_3, $q_3 + dq_3$ is, according to Sommerfeld and Bethe:

$$3\left(\frac{G}{2\pi}\right)^3 \frac{1}{n} dq_1 \, dq_2 \, dq_3 = dZ.$$

(n number of atoms per cc), so that, for the probability of an electron passing from k to $k-q$, we have to form the following integral:

$$\frac{2C^2 q^2}{3\sigma h (2\pi)^3} \int \frac{q^3}{v_{\bar{q}}} f\left(E_{k-q} - E_k + hv_{\bar{q}}\right) d\bar{q}_1 \, d\bar{q}_2 \, d\bar{q}_3$$

Here, σ stands for the density of the crystal $\sigma = n.M.$ The constant G, as is inevitable, has disappeared. We have, further:

$$\bar{q}^2 = \bar{q}_1^2 + \bar{q}_2^2 + \bar{q}_3^2 \quad \text{hence} \quad d\bar{q}_f d\bar{q}_2 d\bar{q}_3 = \bar{q}^2 d\bar{q} \sin \Theta d\Theta d\Phi$$

So the integral becomes

$$\frac{2C^2 q^2}{3\sigma h (2\pi)^3} \int \frac{\bar{q}^3}{v_{\bar{q}}} f\left(E_{k-q} - E_k + hv_{\bar{q}}\right) d\bar{q} \sin \Theta d\Theta d\Phi \quad .$$

and if we then integrate over Θ and Φ and, in place of $\bar{q}$ we introduce the integration variable $U = 2\pi t/h(E_{k-q} - E_k \; h \cdot v_{\bar{q}})$ we obtain

$$\frac{8C^2 q^2}{3\sigma h (2\pi)^2} \cdot \frac{t}{u} \cdot \int \frac{q^2}{v_{\bar{q}}} \cdot \frac{1 - \cos U}{U^2} \, dU.$$

It is generally only at the point $U = 0$ that the integral becomes important, so that the asymptotic value is obtained

$$W(k; \, k-q) = \frac{8C^2 q^4}{2\pi \cdot 3\sigma h v_q \cdot u} \cdot t \quad \text{is obtained.}$$

If we again introduce u in place of q -

$$W(k, \, k-q) = \frac{8C^2 (2\pi v)^3}{3\sigma h u^5} \cdot t$$

Evaluation of the individual values yields approximately

$$\sim 10^{-23} \cdot v^3 \cdot t$$

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This is the number of transitions into the frequency range ν, $\nu + d\nu$

By intergration over ν the number of transitions per second -

$$2.5 \cdot 10^{-28} \nu^4_{max} \sim 10^{25} - 10^{29}.$$

so that for each electron per second 10^3 to 10^7 transitions occur.

Hency the average duration -

$$10^{-8} - 10^{-7} \text{ sec.}$$

The total energy transferred per second is

$$h \int \nu \, W(k, \, k-q) d\nu \sim 10^{10} - 10^{15} \text{ log/sec.}$$

which makes, per electron -

$$10^{-12} - 10^{-7} \text{ erg/sec.}$$

In contrast to this, however, is the almost equal reverse transfer from the lattice to the electron gas. 1/10 e-volt is transferred from one electron in about 10^{-1} to 10^{-6} sec.

    d)   <u>MULTIPLE COLLISIONS WITH THE LATTICE.</u> We mentioned earlier in connection with simple collisions that, by making allowance for higher approximations in the perturbation computation it is possible to take into account the transitions in which one electron and several lattice waves come into contact. These , however, will always be transitions where the electron remains in the same band both before and after the collision. This is because, as a rule the intermediate forbidden zones between the bands are wider than would correspond to one sound quantum of the lattice vibrations; and it is only possible for several sound quanta to combine to form one permitted transition if the intermediate states themselves are permitted, in the first approximation, as transitions. It can thus be seen that consideration of the higher approximations can never give any information about the problem whether energy transfer to the lattice can ever compete with the surrender of energy from the electron gas to the electromagnetic field, since in the latter process the initial and the end states of the electron lie in different bands.

    In the endeavour to find some competing process for this transition other than the electron-lattice transfer of energy, it will therefore be of no use to carry out higher approximations of the Bloch perturbation computation, to say nothing of the difficulty of such an undertaking. It appears, however, that when considering the higher approximations in series development of the lattice potential towards increasing powers of the displacement co-ordinates of lattice molecules, there are produced transitions in which the total energy passes into the lattice and the electron is in another band after the collision. Since the width of the forbidden zones is roughly 50 times that of a sound quantum, we have to look

for collisions in which an electron interacts with about 50 sound quanta.

The potential which operates on the electrons is not strictly periodic with respect to space because, on account of thermal oscillations of the lattice ions, the potential at a definite point in space is continually changing a little with time. Since, however, the movement of the lattice points takes place relatively slowly by comparison with the speed of light, the force acting on the electrons can be looked upon as being determined by the position of the lattice ions at any moment and influences deriving from the velocity of the lattice ions may be disregarded. We shall therefore represent the potential acting on an electron in the lattice as a function of the co-ordinates of this electron and simultaneously as a function of all displacements of the ions from their equilibrium positions. Let the N lattice ions have the 3 N displacement co-ordinates $\xi_1 \, \xi_2 \, \dots \, \xi_{3N}$. We then write the potential V as follows:

$$V = V (x \, y \, z; \, \xi_1 \, \xi_2 \, \dots \, \xi_{3N}).$$

The potential can be developed in a MacLaurin series from the displacement co-ordinates:

$$V(xyz, \xi_1 \dots \xi_{3N}) = \sum \xi_{k_1}^{n_1} \xi_{k_2}^{n_2} \xi_{k_3}^{n_3} \dots \frac{1}{n_1! n_2! n_3! \dots} \frac{\partial^{(n_1 + n_2 + n_3 + \dots)} V}{\partial \xi_{k_1}^{n_1} \partial \xi_{k_2}^{n_2} \partial \xi_{k_3}^{n_3} \dots}$$

Here, the differential quotients must be formed according to the ξ_i at the point $\xi_1 = \xi_2 = \dots \xi_{3N} = 0$, but we will refrain from making any indication of this in the equations.

The displacement co-ordinates can be represented in the familiar way by (complex) normal co-ordinates of the lattice:

$$\xi_i = \sum_1^{3N} \{ q_\rho \gamma_\rho^{(i)} + q_\rho^+ \gamma_\rho^{(i)*} \},$$

so that, by substituting these for the displacement co-ordinates in the MacLaurin series, this series progresses according to quite homogeneous functions of q_i and q_i^+.

If we try to pick out one such term from the series, having the factor

$$q_{\rho_1}^{\rho_1} q_{\rho_2}^{\rho_2} q_{\rho_3}^{\rho_3} \dots \cdot \sum A_{n_1 n_2 n_3} \dots \frac{\partial^{(n_1 + n_2 + n_3 \dots)} V}{\partial \xi_{k_1}^{n_1} \partial \xi_{k_2}^{n_2} \partial \xi_{k_3}^{n_3} \dots}$$

where the sum must be extended over all whole numbers n_1, n_2, n_3 etc. for which the equation $(n_1 + n_2 + n_3 \dots) = (\rho_1 + \rho_2 + \rho_3 \dots)$ is valid, and for all combinations of the numbers $k_1, k_2, k_3 \dots$, where all values can be assumed from the series 1, 2, 3, 4 ... 3N. The values $A_{n_1 n_2 n_3 n_4} \dots$ are constants, the special value of which is of no further interest here.

In the quantum theory, we have to introduce the following matrices for q_i and q_i^+ :

$$(q_i)_{N_i N_i'} = \sqrt{\frac{h}{8\pi^2 \nu_i M}} \sqrt{N_i + 1}\, \partial_{N_i N_i' - 1}\, e^{2\pi i \nu_i t} ,$$

$$(q_i^+)_{N_i N_i'} = \sqrt{\frac{h}{8\pi^2 \nu_i M}} \sqrt{N_i}\, \partial_{N_i N_i' + 1}\, e^{-2\pi i \nu_i t} .$$

Here, M stands for the mass in one lattice unit, ν_i the frequency in the the i order of lattice vibration, N_i a whole number, equal to the number of sound quanta of the frequency ν_i. The first of the two matrices is directly connected with the generation of a sound quantum of frequency ν_i in the lattice, while the second equation corresponds to the emission of a lattice quantum. The first process can also take place when there are no sound quanta present ($N_i = 0$), but the second cannot. Thus there is here, as in the Einstein light quantum theory, the existence of a spontaneous process for the energy transfer electron gas - lattice vibrations, while the reverse process naturally only occurs when it is induced.

If, now, we insert the matrices q_i in the selected term of the MacLaurin series, we obtain immediately

$$\sqrt{\frac{h}{8\pi^2 M}}^{\rho_1 + \rho_2 + \rho_3 + \dots} \left(\frac{1}{\nu_{p_1}^{\rho_1} \nu_{p_2}^{\rho_2} \nu_{p_3}^{\rho_3} \dots} \right)^{\frac{1}{2}} \Pi_i \left\{ \left(\frac{(N_{p_i} + \rho_i)!}{N_{p_i}!} \right)^{\frac{1}{2}} \cdot \partial_{N_{p_i}\, ;\, N_{p_i} + \rho_i} \right\}$$

$$\times X e^{2\pi i t(\rho_1 \nu_{p_1} + \rho_2 \nu_{p_2} + \dots)}$$

in which we have put the value

$$\sum A_{n_1 n_2 n_3} \dots \frac{\partial^{(n_1 + n_2 + n_3 + \dots)} V}{\partial \xi_{k_1}^{n_1} \partial \xi_{k_2}^{n_2} \partial \xi_{k_3}^{n_3} \dots} = X$$

This value X is naturally also a function of the electron co-ordinates.

We shall now make another matrix from this function X, by forming out of two electron eigenfunctions the integral

$$\int d\tau \Psi_k^* X \Psi_{k'} = X_{kk'}$$

This integral can naturally, owing to the periodicity characteristics of all the functions appearing in it, be converted into an integral over a unit of the lattice.

Finally we obtain a matrix element which describes a transition in the electron gas from the state to the state k' and the generation of N_{p_1}

sound quanta of frequency ν_{p_1}; N_{p_2} sound quanta of frequency ν_{p_2}; N_{p_3} sound quanta of frequency ν_{p_3} etc. It would then be necessary to use these matrix elements to form the usual perturbation equation in order to calculate the probability of all these transitions. In a precise analogy to the way in which Bethe and Sommerfeld proceeded for simple collisions we here obtain the equation:

$$\left| c(k,\ k';N_{p_1}+\rho_1;\ N_{p_2}+\rho_2;\ \ldots) \right|^2 = \left(\frac{h}{8\pi^2 M} \right)^{\rho_1+\rho_2+\rho_3+\cdots} \frac{1}{\nu_{p_1}^{\rho_1}\ \nu_{p_2}^{\rho_2}\ \nu_{p_3}^{\rho_3}\cdots}$$

$$\prod_i \frac{(N_{p_i}+\rho_i)!}{N_{p_i}!}\, |X_{kk'}|^2 \cdot 2\, \frac{1-\cos\frac{2\pi Wt}{h}}{\left(\frac{2\pi W}{h}\right)^2}\ ;\quad W = E_k' - E_k + h\, \Sigma\, \rho_i \nu_{p_i}$$

As in previous cases this equation confirms that for large time values, the only probable transitions are those which obey the law of conservation of energy. However the law of conservation of energy will be fulfilled, if k and k' stand for states in different bands of electron energy. It is only necessary for a large number (about 50) of sound quanta to be generated simultaneously in the lattice for the big difference in in energy between the electronic states in the various bands to be covered. The probability of such a transition is then simply proportional to

const $\prod \dfrac{(N_{p_i}+\rho_i)!}{N_{p_i}!}$ and, if we assume that all the frequencies ν_{p_i} are different from each other, the largest term in this expression is given by

$$N_{p_1}\, N_{p_2}\, N_{p_3}\, \ldots$$

Now we have to integrate over all the possible directions of the sound quantum radiation in the space, for each of the various ν_{p_i}, which yields the factor $\nu_{p_i}^2$ for each N_{p_i}. Since, in the equation, each of the ν_{p_i} appears once in the denominator, after integration over all directions there remains one each of the factors ν_{p_i} in the numerator. Thus, the probability of simultaneous collision between an electron and a large number of sound quanta can be put as proportional to

$$(\bar{\nu}\, N_{\bar\nu})^{\frac{\Delta E}{h\bar{\nu}}},$$

where $\bar{\nu}$ represents a mean value of the frequencies participating in the collision and ΔE is the difference in energy between the initial and the end states of the electron.

For temperatures higher than 300°K we may represent the number of sound quanta by the Rayleigh-Jeans Law:

$$N_\mu = \frac{kT}{h\nu},$$

so that for temperatures above room temperature the probability of transition of an electron from one band to another with emission of energy to the lattice becomes

$$W = \text{const.} \left(\frac{kT}{h} \right)^{\frac{\Delta E}{h\nu}}$$

Naturally the constant which has not been calculated here is extraordinarily small. Still, the factor

$$\left(\frac{kT}{h} \right)^{\frac{\Delta E}{h\nu}}$$

will generally make itself very conspicuous and this will be an extremely sudden event as soon as T has become so big that

$$\left(\frac{kT}{h} \right)^{\frac{\Delta E}{h\nu}}$$

has become of the same order as the reciprocal of the unknown constants. From this temperature on, the probability of multiple collisions will increase in such a way that practically all the electron transfers will yield up their energy to the lattice and no longer to the electro-magnetic field. Unfortunately it is not possible to say where this temperature limit lies because it would be essential to know the values of the integral. These are at present unknown and are very difficult to estimate. In general, we suppose it may be expected that these multiple collisions can be observed even at very low temperatures and that they then have the effect of fluorescence quenching. From this we should have to expect fluorescence only in the case of those solids for which the temperature limit is very high. The crystal phosphors are examples of this type of solid. It is also known that heating of the crystal results in a quantitative extinction of the fluorescence process.

We have considered only one possible process which can effect a transfer of energy to the lattice during the transition of an electron from one band to another. Actually, however, there is an extremely large number of possibilities which rest on the fact that, in addition to the quanta in absorption there may be any amount of quanta in emission, which causes the exponent of T to increase substantially. Thus in addition to the expression which we have recorded, there is another factor, namely a function of T, which enters into it, and about which we possess no further information. We therefore have to be content to show that there are processes satisfying the required conditions and the probability of which may assume abnormally high values with an increase in temperature. *

INTERACTION OF ELECTRONS AMONGST EACH OTHER

Apart from their interaction with the lattice, we must also look at the mutual interaction of electrons, which, if the electron concentration is high enough, can similarly bring about a retardation of a fast electron.

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* The unusually short lifetime of the electron in the upper band as a result of the effect of multiple collisions in the case of selected radiators can be estimated from experimental data. See here F.MÖGLICH, N. RIEHL, R. ROMPE, ZS .f.techn. Phys. loc. cit. The significance of multiple collisions for luminophores will be discussed in a paper by the author in Phys. ZS. 41 (1940) 236. See in this connection also N.RIEHL, M. SCHON, ZS. f. Phys. 114 (1939) 682.

This interaction takes place between the fast electron, entering the upper band, and the aggregate of slow electrons which are in temperature equilibrium with the lattice. This is an effect which was studied in detail for plasma in gases and which is due to the existence of the "microfield" (21). Since it is possible also in the case of the gas plasma to describe the microfield interaction of the electrons under the assumption that the ions are practically static, these reasonings can be applied directly to the electrons in the upper band, as long as these can be regarded as not degenerate, i.e. the electron concentration is small by comparison with the number of terms in the band. The quasi-neutrality is ensured in the case of a crystal - if the effect of external electrical fields is disregarded. For the relaxation distance s of a fast electron surrounded by slow electrons, i.e. for the distance which the fast electron must travel before coming to a state of equilibrium, we can assume:

$$ s = \frac{(kT)^2}{2\pi e^4 N} = \frac{1}{6\pi} \frac{m^2 v^4}{e^4 N} \quad . $$

It is probably safe to assume that electron concentrations of 10^{16} to 10^{18} can be produced in the upper band of an insulator, perhaps by radiation (22). These values lead to equilibrium times of 10^{-10} to 10^{-13}. It can be seen that, even for low electron concentrations, times of 10^{-10} are obtained, i.e. much shorter times than those resulting from interaction with the lattice, if the effect of multiple collisions at the higher temperatures is ignored. Hence we are of the opinion that the plasma interaction of the electrons amongst each other is the process leading to equilibrium of the electrons in the upper band within the meaning of the results obtained by Birus and Schön based on the fact that no band-to-band fluorescence is observed shorter than 10^{-8} sec. The equilibrium process of a fast electron in the upper band probably takes place in the following manner: When the temperature is low, the energy of the fast electron is first distributed by means of the electronic interaction to all the electrons present in the upper band, which then in their turn give up the energy to the lattice in single impacts. This last process is again a fairly rapid one, because there are very many electrons taking part in it simultaneously. At higher temperatures there may appear some competition between the plasma electronic interaction and the multiple collisions and this will finally prove decisive in favour of the latter. In this case, however, the electrons leave the upper band entirely.

When applying the plasma interaction to solids, the following must be observed: It might be assumed at first that all available electrons - that is those in the lower band also - are involved in the mutual interaction of the electrons and that therefore an electronic concentration of 10^{23} must be reckoned with. This would result in an equilibrium period (constant) of 10^{-16} sec for a 1-volt electron. This assumption is not tenable, however, because the plasma interaction is only available for those electrons capable of taking up energy. Owing to the Pauli prohibition, however, there are at best only as many electrons capable of this in the lower band, as there are holes resulting from absorption. Consideration of the total number would thus introduce a factor 2 in the equilibrium time.

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It is only if the fact electrons possess energy which is great
compared with the energy gap between the two bands (for instance
in the case of radiation of short wave ultra violet), that there could
be a greater participation of the electrons of the lower band,
because these could then absorb enough energy to enable them to get
past the forbidden zones.   Of course such fast electrons would
probably fall within the range of the strong activity of the multiple
collisions ($E: h\bar{v}$ very large) and return to the lower band without
radiation.   Nevertheless it cannot be proved quite so easily that it
is just such processes which are responsible for the excitation of
insulators by means of fast electrons or alpha-particles.

On the other hand, with metals a large number of electrons can
always participate in plasma interaction because of course the lower
band is only half full, so that very short relaxation times may be
expected for them.

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