Progress of Theoretical Physics, Vol. 12, No. 4 October 1954

Theory of the Electronic Polaron and Ionization of a Trapped Electron by an Exciton

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(Received June 19, 1954)

Introducing the concept of the electronic polaron which is an analogue of the usual lattice polaron, we have considered its motion under the influence of a trapping potential, by using a simplified model for the electronically polarizable crystal such that the excited states of crystal electrons consist of a single exciton band. By a suitable transformation we obtain an expression for the Hamiltonian which consists of the following three parts: the first part describes the motion of an electron under the potential in an dielectric medium in the classical way, the second part represents the energy of the electronic polarization field the quanta of which are nothing but free excitons, and the last part is the interaction energy between these two parts which causes the production or annihilation of excitons in the neighbourhood of the potential by exchanging energy with the electron. Treating the last part as a perturbation, we have calculated the probability for the ionization of a trapped electron by an exciton. After correcting the oversimplification of the model, we have applied the obtained result to actual crystals, leading to a conclusion that in alkali-halides the excitons annihilate rather by ionizing *F*-electrons than by spontaneous emission if the density of the *F*-centers is larger than 10^{16} per c.c., in consistence with the experimental results of Apker and Taft on the external photoelectric effect.

§ 1. Introduction and basic idea

The interaction of a conduction electron with lattice vibrations in an ionic crystal has been investigated very actively of late years,[1)-3)] because of its theoretical and practical importances, as well as its mathematical interest and difficulty. When the velocity of the electron is so slow that no phonon can be emitted, we can visualize the *stationary state* of the system by considering the electron, clothed with the polarization or virtual phonons around itself, to move freely in the crystal with a self-energy and a corrected effective mass both of which are the main subjects of the so-called *polaron* problem (we are considering only the case of the absolute zero of temperature). On the other hand, when the velocity of the electron exceeds some critical value characteristic of the crystal, the stationary state description is no longer appropriate; we should treat the interaction to be responsible for the *transition* of the electron between different states, though in actual crystals such as alkali-halides the interaction is so strong that the above statement has only an approximate meaning.

Now, as is well known, the general polarization consists of two parts: "displacement polarization" or lattice polarization as state above on the one hand, and "electronic polarization" on the other hand, the latter being more general as it plays a rôle also in non-polar crystals where the former does not. A conduction electron in an insulator or a semiconductor interacts also with the electronic polarization of the crystal, thus leading to the concept of the "electronic polaron"[4] analogous to the usual or "lattice polaron" stated above. For the ordinary velocities of the electron, the electronic polarization induced around it is generally considered to follow the motion of the electron almost perfectly, thus it is the usual method of description[5] to consider the electron as a classical point charge imbedded in a medium with a dielectric constant κ_0 which is to be identified with the optical dielectric constant of the crystal. As we have shown previously,[6] this description corresponds to the quantum mechanical adiabatic approximation between the conduction and the crystal electrons. In the electronic polaron theory the point charge has to be replaced by somewhat spread cloud of charge due to uncertainty principle as in the case of a lattice polaron.[1] Now, in our case too, there is a critical velocity of the electron beyond which the electronic polarization cannot follow the electron, or the stationary state description is inappropriate. If there is any analogy or parallelism between the electronic and lattice polarizations, the electron with such high velocities can emit *quanta of electronic polarization*, and we have intimate connection between the electronic polaron state and the processes such as emission and absorption of these quanta by the electron, both of which are to be treated under a unified formulation in the same way as the scattering of an electron by lattice vibrations is considered to be nothing but another aspect of the lattice polaron problem.

What is meant by the "quanta of electronic polarization" is easy to understand if we consider in analogy with the case of an isolated atom. In insulating and semiconducting crystals, we should take them as the excitation of filled band electrons to the conduction band or the exciton levels if any. It is qualitatively inferred from perturbation theory that the narrower the energy gap between the filled and conduction band is, the more easily the crystal can be polarized. In fact, there is substantially an antiparallelism between high frequency dielectric constant κ_0 and the gap energy $\mathcal{E}$ for many crystals of different types, as is seen from Tab. 1. Roughly speaking the gap energy $\mathcal{E}$ in this case plays the same rôle as the phonon energy $\hbar\omega$ does in case of the lattice polaron, and the relaxation time of the electronic polarization is given by

Tab. 1. Gap energies ε and optical dielectric constants κ_0 of various crystals

	ε(eV)	κ_0
NaCl	9.6	2.25
MgO	6	2.95
diamond	5.5	5.85
AgCl	5	4.01
BaO	4.8	4
Si	1.1	12.5
Ge	0.8	18.5

$$\tau \sim \hbar/\mathcal{E}\,.$$

It is interesting to note that the interaction of the conduction electron with the electronic polarization in an insulating crystal is analogous to the interaction of a free electron with vacuum polarization[7] which is caused by the virtual creation of pairs of an electron and a positron. The most essential difference lies in the circumstance that a conduction electron in a crystal, if its velocity is sufficiently large, can emit pairs of another conduction electron and a positive hole, while it is impossible for a free electron in vacuum to create pairs of an electron and a positron except in the neighbourhood of a strong field such as is produced by a nucleus, as is evident from the Lorentz invariance.

Owing to the complexity of the band structures and the lack of the accurate knowledge on the band wave functions in actual crystals, it seems very difficult to treat quantitatively the interaction stated above. In this work we take a model as simple as possible without spoiling the most essential aspect of the problem.

First of all we assume only one exciton band for the excited states of the crystal electrons, instead of the series of exciton bands and an ionization continuum. It is true that this model is inappropriate to the discrimination between the production of excitons and the ionization of filled band electrons to the conduction band*, but it is convenient for our present aim, which consists in discussing the electronic polaron problem in connection with the annihilation and production of an exciton by an electron. With this model we shall derive, in § 2, the Hamiltonian for the system composed of crystal electrons and an additive electron, which has a form characteristic of the Hamiltonian for the system of a particle and a boson field.

One of the subjects which are interesting in case of the electronic polaron problem is to see whether and how the classical picture of a conduction electron as a point charge in a dielectric medium is derived from general formulation. For this purpose it is convenient to consider a fixed charge distribution due to any kind of imperfection which interacts with the electron in the field of the electronic polarization. In § 3 we set up the Hamiltonian for this system by making use of the result obtained in § 2, and then express it in the new variables by a suitable transformation so as to derive the classical picture stated above. The new expression thus obtained of the Hamiltonian has diagonal elements which correspond to the two independent systems, one for the electronic polaron moving under the influence of the potential due to the imperfection with a shielding factor $1/\kappa_0$, the other for the free excitons or the electronic polarization waves, the origin of whose co-ordinates are somewhat modulated near the imperfection. The expression has also off-diagonal elements corresponding to the interaction between the two systems in the neighbourhood of the imperfection.

Treating the last term as a perturbation, we have calculated, in § 4, the transition probability for the process in which a free exciton annihilates near the imperfection by giving its energy to the trapped electron (strictly speaking, the electronic polaron) and ionizing it.

The oversimplification of the model on which we have formulated the above method can be corrected by connecting the interaction constant with the oscillator strength of the exciton transition so as to be applicable to real crystals. This is done in § 5, the result of which tells us, for instance, that in alkali-halides an exciton annihilates by ionizing *F*-center electrons instead of emitting radiation spontaneously if the density of the *F*-centers is larger than 10^{16}/c.c. This is in accordance with the experimental results by Apker and Taft[10-11] on the one hand, and explains to some extent, as Seitz[12] has been

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* For these two processes, Kubo and Takano[8] calculated the transition probabilities, using Wannier's wave function[9] for the exciton states

expecting, the absence of emission by an exciton from any experiment carried out so far, on the other hand.

§ 2. The electronic polarization as a boson field

Let us consider an insulating crystal C, and take into account the motion of *valence* electrons only which are responsible for the most part of the electronic polarization, the *inner* electrons and the nuclei being considered as the sources of the potential for the former. Denoting the coordinates of the valence electrons by $\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots$ and $\boldsymbol{r}_N$, we can set up the Hamiltonian H_C for these N-electrons. In addition to this system we consider an *extra* electron e to be introduced into the conduction band of the crystal. The Coulomb interaction of e with the valence electrons is denoted by

$$U(\boldsymbol{r}\,;\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N) = \sum_{i=1}^{N} e^2/|\boldsymbol{r}-\boldsymbol{r}_i|, \tag{2·1}$$

and the interaction of e with the inner electrons and the nuclei of the crystal, together with the kinetic energy of e itself, is written as H_0. Thus the total Hamiltonian takes the form:

$$H = H_0(\boldsymbol{r}) + H_C(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N) + U(\boldsymbol{r}\,\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N). \tag{2·2}$$

Now, the system C of N-electrons, in the one body approximation, has excited states in which some of the electrons are excited to the conduction band, but in the next approximation, in which the interaction of the excited electrons and their counterparts—the positive holes—is taken into account, we have to consider a series of the exciton bands below the ionization continuum stated above. In ionic crystals these exciton bands play a very important rôle in some phenomena. Let us assume, for simplicity, that the excited states of the N-electrons as a whole can be represented by *a single exciton band*, each exciton having an energy $\mathcal{E}$ irrespective of its wave number $\boldsymbol{w}$. Then the eigenstates of the system C can be specified by the number n_w of excitons for each $\boldsymbol{w}$, and we can write

$$\begin{aligned} &H_C \Psi(\cdots, n_w, \cdots, n_{w'} \cdots | \boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N) \\ &\quad = (E_0 + \mathcal{E} \sum_w n_w) \Psi(\cdots, n_w, \cdots, n_{w'}, \cdots | \boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N). \end{aligned} \tag{2·3}$$

The above consideration, of course, is valid only when the total number of excitons $\sum_w n_w$ is much smaller than N.

The next procedure is to find the matrix elements of U in the $\{n_w\}$ representation. For this purpose we take a tightly bound atomic orbital approximation[13] for the wave function Ψ. Denoting the ground and excited states of an isolated atom by $\phi^g(\boldsymbol{r})$ and $\phi^e(\boldsymbol{r})$, respectively, we construct a normalized Slater determinant

$$\Phi(m_1, m_2,\cdots, m_n|\boldsymbol{r}_1, \boldsymbol{r}_2,\cdots, \boldsymbol{r}_N)$$

$$=\frac{1}{\sqrt{N!}}\begin{vmatrix} \phi^g(\boldsymbol{r}_1-\boldsymbol{R}_1) & \phi^g(\boldsymbol{r}_2-\boldsymbol{R}_1) & \cdots\cdots\cdots\cdots\cdots\cdots \\ \phi^g(\boldsymbol{r}_1-\boldsymbol{R}_2) & \phi^g(\boldsymbol{r}_2-\boldsymbol{R}_2) & \cdots\cdots\cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots & \cdots\cdots\cdots & \cdots\cdots\cdots\cdots\cdots\cdots \\ \phi^e(\boldsymbol{r}_1-\boldsymbol{m}_1) & \phi^e(\boldsymbol{r}_2-\boldsymbol{m}_1) & \cdots\cdots\cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots & \cdots\cdots\cdots & \cdots\cdots\cdots\cdots\cdots\cdots \\ \phi^e(\boldsymbol{r}_1-\boldsymbol{m}_2) & \phi^e(\boldsymbol{r}_2-\boldsymbol{m}_2) & \cdots\cdots\cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots & \cdots\cdots\cdots & \cdots\cdots\cdots\cdots\cdots\cdots \\ \phi^g(\boldsymbol{r}_1-\boldsymbol{R}_N) & \phi^g(\boldsymbol{r}_2-\boldsymbol{R}_N) & \cdots\cdots\cdots\cdots\cdots\cdots \end{vmatrix} \qquad (2\cdot4)$$

for the state in which the m_1-th, m_2-th,$\cdots$ and m_n-th atoms of the crystal are excited. We have written $\boldsymbol{m}_1$, $\boldsymbol{m}_2,\cdots$ instead of $\boldsymbol{R}_{m1}$, $\boldsymbol{R}_{m2},\cdots$ for the sake of simplicity. The overlaps between all pairs of atomic orbitals are neglected. The eigenstates of H_C are such that each of the excited positions (for example, m_1) propagates from atom to atom with a definite wave number, and these excitation waves can be taken as independent of each other if the total number n of excitons is much smaller than N as has been assumed above; because the effect of the coincidence of m_i and m_j for $i \neq j$ (a collision between two excitons) can be neglected for such cases. Thus the normalized eigenfunctions Ψ of H_C can be written down as follows:

$$\Psi(\cdots, n_w,\cdots, n_{w'},\cdots|\boldsymbol{r}_1, \boldsymbol{r}_2,\cdots, \boldsymbol{r}_N)$$

$$=\{N^n \prod_w (n_w!)\}^{-1/2} \sum_{m1}\sum_{m2}\cdots\sum_{m_n} \exp\left[\sum_w i\boldsymbol{w}\cdot(\boldsymbol{m}_{w1}+\boldsymbol{m}_{w2}+\cdots+\boldsymbol{m}_{w,n_w})\right]$$

$$\times\,\Phi(m_1, m_2,\cdots, m_n|\boldsymbol{r}_1, \boldsymbol{r}_2,\cdots, \boldsymbol{r}_N),^* \qquad (2\cdot5)$$

$$\sum_w n_w = n.$$

In this expression the sets of $\{m_{w,1}, m_{w,2},\cdots, m_{w,n_w}\}$ for *all* w's coincide with $\{m_1, m_2,\cdots, m_n\}$, as a whole; we have only to allow the latter elements to each wave number, n_w elements being assigned to the wave number $\boldsymbol{w}$.

Now that the explicit form of Ψ is known, we can calculate the matrix elements of the Coulomb interaction U. Using (2·1) and (2·5), we have

$$(\cdots, n_w,\cdots, n_{w'},\cdots|U|\cdots, n'_w,\cdots, n'_{w'},\cdots)$$

$$=\{N^n \prod_w (n_w!)\}^{-1/2}\{N^{n'} \prod_w (n'_w!)\}^{-1/2}$$

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* In the previous report (letters to the edditor) the author has restricted the values of n_w to 0 and 1 only, leading to the Hamiltonian in which the creation and annihilation operators are those for the Fermions. Although it makes no difference so far as the results obtained in this work are concerned whether we use the Fermion or Boson operators, there is no reason in principle for the restriction of n_w values. The author is indebted to Professor H. Fröhlich who has kindly suggested to him that the exciton should be treated as a Boson.

$$\times \sum_{m_1} \cdots \sum_{m_n} \sum_{m_1'} \cdots \sum_{m'_n} \exp[\sum_{w} i\boldsymbol{w} \cdot (m'_{w,1} + \cdots + m'_{w,n'_w} - m_{w,1} - \cdots - m_{w,n_w})]$$

$$\times \sum_{i=1}^{N} \int \frac{e^2}{|\boldsymbol{r} - \boldsymbol{r}_i|} \Phi^* (m_1, \cdots, m_n | \boldsymbol{r}_1, \cdots, \boldsymbol{r}_N) \Phi (m_1', \cdots, m'_{n'} | \boldsymbol{r}_1, \cdots, \boldsymbol{r}_N) \prod_{i=1}^{N} d\boldsymbol{r}_i . \tag{2·6}$$

The last integral is different from zero in the following three cases:

(i) $n = n'$ and the set $(m_1, m_2, \cdots, m_n)$ as a whole coincides with $(m_1', m_2', \cdots, m'_{n'})$.

(ii) $n+1 = n'$ and the $(m_1, m_2, \cdots, m_n)$ as a whole coincides with $(m_1', m_2', \cdots, m'_{j-1}, m'_{j+1}, \cdots, m'_{n'})$, where j may take any one of $(1, 2, \cdots n')$.

(iii) The reverse case of (ii).

In case (i), we have the electrostatic potential at the position $\boldsymbol{r}$ due to the N-electrons, those which belong to the m_1-th, m_2-th, $\cdots$ or m_n-th atom being excited. Now the charge distribution

$$|\phi^e(\boldsymbol{r})|^2 - |\phi^g(\boldsymbol{r})|^2$$

has neither a total charge nor a dipole moment, because both wave functions are of atomic type and have definite parities. If we take account of the point and dipole potentials only, and neglect the potentials of the higher multipoles we can equate the integral in (2·6) to that integral in which the ground state wave function Φ_0 of H_C (no excited atoms) is substituted. Then the summation over $(m_1, m_2, \cdots, m_n)$ leads to a non-zero value only when the set $(m'_{w,1} \cdots, m'_{w,n'_w})$ as a whole coincides with the set $(m_{w,1}, \cdots, m_{w,n_w})$ for each $\boldsymbol{w}$. In the case (i), therefore, we have non-zero matrix elements only when $n_w = n'_w$ for all $\boldsymbol{w}$'s, moreover their values are all equal:

$$\begin{aligned} &(\cdots, n_w, \cdots, n_{w'}, \cdots | U | \cdots, n_w, \cdots, n_{w'}, \cdots) \\ &= (0, 0, \cdots | U | 0, 0, \cdots) = U_0(\boldsymbol{r}). \end{aligned} \tag{2·7}$$

In case (ii) the integral in (2·6) can be calculated, in the approximation stated above, as

$$\begin{aligned} &\sum_{i=1}^{N} \int \frac{e^2}{|\boldsymbol{r} - \boldsymbol{r}_i|} \Phi^* (m_1, \cdots, m_n | \boldsymbol{r}_1, \cdots, \boldsymbol{r}_N) \Phi (m_1, \cdots, m_n, m_j' | \boldsymbol{r}_1, \cdots, \boldsymbol{r}_N) \prod_{i=1}^{N} d\boldsymbol{r}_i \\ &\quad = \frac{N(N-1)!}{N!} e \varphi_{m'_j}(\boldsymbol{r}), \end{aligned} \tag{2·8}$$

where $\varphi_{m'_j}(\boldsymbol{r})$ is the potential due to the dipole moment μ located at the m_j'-th atom, μ being given by

$$\mu = \int \phi^{g*}(\boldsymbol{r}) e \boldsymbol{r} \phi^e(\boldsymbol{r}) d\boldsymbol{r}, \tag{2·9}$$

that is, the dipole-moment for the atomic transition. The summation over $m_1, m_2, \cdots$ and m_n (m_j' being fixed) leads to a non-zero valve only when $n'_w = n_w$ for all $\boldsymbol{w}$'s except the wave number to which m_j' belongs. For the latter wave number we have necessarily

$n'_w = n_w + 1$. Paying attention to the fact that j can take any of $(1, 2, \cdots, n_w+1)$, we see that

$$(\cdots, n_w, \cdots, n_{w'}, \cdots | U | \cdots, n_w+1, \cdots, n_{w'}, \cdots)$$

$$= \frac{e}{\sqrt{N}} \sqrt{n_w+1} \sum_m \exp(i\boldsymbol{w}\cdot\boldsymbol{m})\, \varphi_m(\boldsymbol{r}). \tag{2·10}$$

Let us now assume more explicit forms for the atomic wave functions ϕ^g and ϕ^e. In order that the exciton absorption is permitted optically, ϕ^g has to be of different parity from ϕ^e. If ϕ^g is of the s-type, we have to consider triply degenerate p-orbitals for ϕ^e, which necessarily lead to three types of excitation waves. As Heller and Marcus[14] have shown, the approximate eigenstates resulting from this degeneracy are *one longitudinal* and *two transverse* waves for each $\boldsymbol{w}$, where the "longitudinal" means that the p-state which propagates from atom to atom with wave number $\boldsymbol{w}$ should itself be directed toward $\boldsymbol{w}$, the "transverse" corresponding to the p-states directed perpendicular to $\boldsymbol{w}$. Then the summation in (2·10), when it is replaced by the integration, vanishes for the transverse waves; that is, in this approximation the transverse exciton waves do not interact with the extra electron. For the longitudinal waves (2·10) can be calculated as

$$(-e)/\sqrt{L^3}\cdot\gamma\cdot i/w\cdot\sqrt{n_w+1}\exp(i\boldsymbol{w}\cdot\boldsymbol{r}),$$

where

$$\gamma = 4\pi e\mu/\sqrt{v_0}. \tag{2·11}$$

and L^3, v_0 and μ mean the volume of the crystal, the volume of a unit cell and the absolute value of μ given by (2·9), respectively.

The matrix elements in case (iii) can be calculated as the conjugate complexes of those in case (ii), and finally, introducing the annihilation and production operator b_w and b_w^* for a boson;

$$b_w = \begin{bmatrix} 0 & \sqrt{1} & 0 & 0 & \cdots\cdots \\ 0 & 0 & \sqrt{2} & 0 & \cdots\cdots \\ 0 & 0 & 0 & \sqrt{3} & \cdots\cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots\cdots \end{bmatrix}_w, \quad etc. \tag{2·12}$$

we can express U in the $\{n_w\}$ representation:

$$U(\boldsymbol{r};\, \boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N) \equiv U_0(\boldsymbol{r}) + (-e)\varphi(\boldsymbol{r}), \tag{2·13}$$

$$\varphi(\boldsymbol{r}) = \gamma/\sqrt{L^3}\cdot\sum_w i/w\,\{b_w \exp(i\boldsymbol{w}\cdot\boldsymbol{r}) - b_w^* \exp(-i\boldsymbol{w}\cdot\boldsymbol{r})\}. \tag{2·14}$$

$U_0(\boldsymbol{r})$ is the potential energy for the extra electron e when the crystal electrons are in the ground state as is seen from the definition (2·7), thus it will be quite evident that $\varphi(\boldsymbol{r})$ is to be interpreted as the electrostatic potential due to the electronic polarization which is caused by the deviation of $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N)$ from $\Phi_0(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N)$, if we call to mind the above approximation in which we have taken into account only up to the dipole potential.

The above expression is not altered, when the situation is reversed such that the ground state of the atom consists of triply degenerate p-orbitals all being filled with electrons and the excited state is of s-type. In either case, after dropping from H_C the energy of transverse exciton waves which do not interact with e, we can write the Hamiltonian for the system as follows:

$$H=\{H_0+U_0(\boldsymbol{r})\}+\{E_0+\mathcal{E}\sum_w b_w^* b_w\}+(-e)\varphi(\boldsymbol{r}). \tag{2·15}$$

The first is the Hamiltonian for the extra electron e under the periodic potential of the crystal when the crystal electrons are fixed to the ground state, so that the eigenstates constitute the conduction band of the crystal in which the electronic polarizability of the crystal is not yet taken into account. If we apply the Wannier-Slater[15] formulation for the perturbed periodic potential problem, under the assumption that $\varphi(\boldsymbol{r})$ is slowly varying perturbation (which is justified for the long wave-length components of $\varphi(\boldsymbol{r})$ in (2·14)), we can simplify (2·15) to the form

$$H=\boldsymbol{p}^2/2m+\mathcal{E}\sum_w b_w^* b_w+(-e)\varphi(\boldsymbol{r}) \tag{2·16}$$

after dropping the unimportant terms, where m means the effective mass of the conduction band, that is:

$$\begin{aligned}\{H_0+U_0(\boldsymbol{r})\}\psi_k(\boldsymbol{r})&=E(\hbar\boldsymbol{k})\psi_k(\boldsymbol{r}),\\ E(\boldsymbol{p})&=E(0)+\boldsymbol{p}^2/2m+(\boldsymbol{p}^4).\end{aligned} \tag{2·17}$$

The Hamiltonian (2·16), combined with (2·14), means that the electronically polarizable crystal behaves as if it were a Boson field, in regards not only to its proper energy structure but also to the interaction with an extra electron. Moreover the interaction energy is of the same form as that of the interaction between an electron and the longitudinal modes of optical lattice vibrations in ionic crystals, which was to be expected because both types of polarization are equivalent from the stand-point of macro-scopic electrostatics. According to our simplified model, the interaction constant γ is to be connected with the dielectric constant κ_0 at high frequencies by the relation

$$\gamma^2=2\pi\mathcal{E}(1-1/\kappa_0), \tag{2·18}$$

the proof of which is given in the Appendix I.

§ 3. The motion of an electronic Polaron under the influence of a trapping potential

The Hamiltonian (2·16) and (2·14) obtained in the preceding section show that the low-lying energy levels of the system constitute the "electronic polaron" band in which the electron moves freely in the crystal accompanied by the electronic polarization around itself. While the mathematical structure of the Hamiltonian is the same as that for the usual (lattice) polaron, the phonons in the latter case are to be replaced by the excitons in the former. We are interested, however, mainly in the behavior of the electronic polaron in the neighbourhood of the trap, so that we proceed directly to a general case. That is, we consider a system composed of three parts: the electronically polarizable crystal C, an extra electron e, and an imperfection Q which may be an ion vacancy or an impurity ion. If we assume that Q is represented by an extra charge distribution $\rho(\boldsymbol{r})$, its interaction $V(\boldsymbol{r})$ with e is given by a Poisson equation

$$\Delta V(\boldsymbol{r})=4\pi e\rho(\boldsymbol{r}) \qquad (e>0), \tag{3·1}$$

and the interaction H_{p} of Q with crystal electronic polarization field is given by

$$H_{\mathrm{p}}=\int \rho(\boldsymbol{r})\varphi(\boldsymbol{r})\,d\boldsymbol{r}=\frac{\gamma}{\sqrt{L^3}}\sum_w \frac{i}{w}\{\rho_w b_w-\rho_w^* b_w^*\}, \tag{3·2}$$

where we have used the equation (2·14) and the definition of ρ_w:

$$\rho_w=\int \rho(\boldsymbol{r})\exp(i\boldsymbol{w}\cdot\boldsymbol{r})\,d\boldsymbol{r}. \tag{3·3}$$

Combining the above with the result obtained in the last section, the energy of the total system can be written down as

$$H=H_e+H_C+H_I+H_{\mathrm{p}}+V(\boldsymbol{r}), \tag{3·4}$$

where we have used the abbreviations H_e, H_C and H_I for the first, second and third terms in (2·16).

The third and fourth parts of the expression (3·4) contain linear terms in the polarization co-ordinates b_w and b_w^*, but the most convenient description appealing to our intuition is such that in the first approximation the electron clothed with electronic polarization moves in the field due to the fixed charge $\rho(\boldsymbol{r})$, the latter also polarizing the surrounding medium. In order to realize this picture from (3·4), it is a natural method to seek an appropriate unitary transformation so that the interaction terms such as H_I and H_{p} disappear. Such a transformation, for the first time, was used by Bohm and Pines[16] for the interaction of electrons and lattice vibrations in metals, and was applied by Morita and Horie[2] to the lattice polaron problem in ionic crystals.

In our case the transformation should be as follows. By a suitable unitary transformation

$$\begin{aligned}\boldsymbol{p}&=\exp(-iS/\hbar)\,\boldsymbol{P}\exp(iS/\hbar),\\ \boldsymbol{r}&=\exp(-iS/\hbar)\,\boldsymbol{R}\exp(iS/\hbar),\\ b_w&=\exp(-iS/\hbar)\,B_w\exp(iS/\hbar),\end{aligned} \tag{3·5}$$

we turn from old variables $\boldsymbol{p}$, $\boldsymbol{r}$ and b_w's to new ones $\boldsymbol{P}$, $\boldsymbol{R}$ and B_w's, in terms of which we now try to express the total Hamiltonian H;

$$H=\exp(-iS/\hbar)\,\Lambda\exp(iS/\hbar)$$

$$
\begin{aligned}
&=\exp(-iS/\hbar)\,\{\Lambda_e+\Lambda_C+\Lambda_I+\Lambda_\rho+V(\boldsymbol{R})\}\exp(iS/\hbar)\\
&=\Lambda_e+\Lambda_C\\
&\quad -i/\hbar\cdot[S,\ \Lambda_e+\Lambda_C]+\Lambda_I+\Lambda_\rho\\
&\quad -1/2\hbar^2\cdot[S,\ [S,\ \Lambda_e+\Lambda_C]]-i/\hbar\cdot[S,\ \Lambda_I+\Lambda_\rho]+\cdots\\
&\quad +V(\boldsymbol{R})-i/\hbar\cdot[S,\ V(\boldsymbol{R})]+\cdots, \qquad (3\cdot6)
\end{aligned}
$$

where Λ with any suffix means the transform of the Hamiltonian H with the same suffix, and is obtained by formally putting new variables in place of the corresponding old ones in the expression H. The operator S is chosen in such a way that the second line in the right-hand side of (3·6) vanishes:

$$-i/\hbar\cdot[S,\ \Lambda_e+\Lambda_C]+\Lambda_I+\Lambda_\rho=0. \qquad (3\cdot7)$$

Then the expression (3·6) reduces to

$$H=\Lambda_e+\Lambda_C+V(\boldsymbol{R})-i/2\hbar\cdot[S,\ \Lambda_I+\Lambda_\rho]-i/\hbar\cdot[S,\ V(\boldsymbol{R})]+\cdots. \qquad (3\cdot8)$$

Now, the equation (3·7) is satisfied by

$$
\begin{aligned}
S&=S_I+S_\rho\\
&=-\frac{e\gamma\hbar}{\sqrt{L^3}}\sum_w\frac{1}{w}\left[\frac{B_w}{\varepsilon+\frac{1}{2m}(-2\hbar\boldsymbol{w}\cdot P+\hbar^2w^2)}\exp(i\boldsymbol{w}\cdot\boldsymbol{R})\right.\\
&\qquad\left.+\exp(-i\boldsymbol{w}\cdot\boldsymbol{R})\frac{B_w^*}{\varepsilon+\frac{1}{2m}(-2\hbar\boldsymbol{w}\cdot P+\hbar^2w^2)}\right]\\
&\qquad+\frac{\gamma\hbar}{\varepsilon\sqrt{L^3}}\sum_w\frac{1}{w}(\rho_wB_w+\rho_w^*B_w^*). \qquad (3\cdot9)
\end{aligned}
$$

Physical meanings of the two parts are as follows: S_I is an operator by which the electron e becomes clothed with electronic polarization, while S_ρ is that which corresponds to the displacement of the origin of the polarization co-ordinates b_w, the new origin being the equilibrium position of static polarization around the charge distribution $\rho(r)$.

In calculating the commutators appearing in (3·8), we can take advantage of the following situation. In the lattice polaron problem there are finite average number of thermal phonons for each mode of vibration so far as the temperature is not absolutely zero, while in our case the energy of each exciton is so much larger than the thermal energy kT that the existence of thermal exciton is out of the question. Even if we treat those processes in which excitons are produced or destroyed, as we do in § 4, the total number of excitons in the initial or final state is limited to a very few number, while the volume L^3 of the crystal is practically infinite. This situation can be expressed mathematically by the relations

$$\langle B_w^* B_w\rangle_w = 0(1/L^3),$$
$$\langle B_w B_w^*\rangle_w = \langle 1 + B_w^* B_w\rangle_w = 1 + 0(1/L^3), \tag{3·10}$$

in which $\langle\ \rangle_w$ means the average over all wave numbers $\boldsymbol{w}$.

If we take the continuum approximation, that is, make the limit w_0 of wave numbers tend to infinity, explicit calculations of the commutators become easier, and we get the following results:

$$-\frac{i}{2\hbar}[S_I, \Lambda_I] = -\frac{e^2\gamma^2}{L^3}\sum_w \frac{1}{w^2}\frac{1}{\mathcal{E} + \frac{1}{2m}(-2\hbar\boldsymbol{w}\cdot\boldsymbol{P} + \hbar^2 w^2)}$$
$$= -\alpha\mathcal{E}\sin^{-1}(P/u)/(P/u)$$
$$= -\alpha\mathcal{E} - \alpha/6\cdot P^2/2m + 0(P^4), \tag{3·11}$$

where u and α are defined by

$$\hbar^2 u^2/2m = \mathcal{E}, \qquad \alpha = 1/2\cdot(1 - 1/\kappa_0)e^2 u/\mathcal{E}, \tag{3·12}$$

and

$$-\frac{i}{2\hbar}[S_\rho, \Lambda_I] = \frac{e\gamma^2}{2\mathcal{E}L^3}\sum_w \frac{1}{w^2}\{\rho_w^* \exp(i\boldsymbol{w}\cdot\boldsymbol{R}) + \rho_w \exp(-i\boldsymbol{w}\cdot\boldsymbol{R})\}$$
$$= -\frac{1}{2}\left(1 - \frac{1}{\kappa_0}\right)V(\boldsymbol{R}), \tag{3·13}$$

$$-\frac{i}{2\hbar}[S_I, \Lambda_\rho] = \frac{e\gamma^2}{2L^3}\sum_w \frac{1}{w^2}\left\{\frac{\rho_w^*}{\mathcal{E} + \frac{1}{2m}(-2\hbar\boldsymbol{w}\cdot\boldsymbol{P} + \hbar^2 w^2)}\exp(i\boldsymbol{w}\cdot\boldsymbol{R}) + \text{h.c.}\right\}$$
$$= -1/2\cdot(1 - 1/\kappa_0)V(\boldsymbol{R}) + \cdots, \tag{3·14}$$

where the omitted terms contain the products of the second or higher derivatives of $V(\boldsymbol{R})$ with the second or higher powers of $\boldsymbol{P}$, and are not of primary importance as far as the potential $V(\boldsymbol{R})$ is rather slowly varying. It is interesting to note that each of the cross commutators (3·13) and (3·14) contributes a half to the shielding effect

$$-(1 - 1/\kappa_0)V(\boldsymbol{R})$$

of the potential $V(\boldsymbol{R})$ by electronic polarization. The next commutator

$$-\frac{i}{2\hbar}[S_\rho, \Lambda_\rho] = -\frac{\gamma^2}{\mathcal{E}}\frac{1}{L^3}\sum_w \frac{1}{w^2}\rho_w^*\rho_w$$
$$= -\frac{1}{2}\left(1 - \frac{1}{\kappa_0}\right)\int \rho(\boldsymbol{r})\frac{V(\boldsymbol{r})}{(-e)}d\boldsymbol{r} = -\mathcal{E}_\rho \tag{3·15}$$

is nothing but the electrostatic energy due to the electronic polarization produced by the field of charge distribution $\rho(\boldsymbol{r})$. Finally the commutator with $V(\boldsymbol{R})$ is calculated as

$$-i/\hbar\cdot[S, V(\boldsymbol{R})] = -i/\hbar\cdot[S_I, V(\boldsymbol{R})]$$

$$=\frac{e\gamma\hbar^2}{m\sqrt{L^3}}\sum_w \frac{1}{\left(\varepsilon+\dfrac{\hbar^2 w^2}{2m}\right)^2}\frac{\boldsymbol{w}}{w}\cdot\text{grand } V(\boldsymbol{R})\,\{B_w \exp(i\boldsymbol{w}\cdot\boldsymbol{R})+B_w^* \exp(-i\boldsymbol{w}\cdot\boldsymbol{R})\} +\cdots\cdots, \tag{3·16}$$

where we have expanded the operator S_I in power series in $\boldsymbol{P}$ and omitted unimportant terms.

The transformation (3·9) which we have chosen is the most appropriate one especially from the physical point of view, for it gives a Hamiltonian which corresponds, in the zeroth approximation, to the classical description of an electron in a dielectric medium, as is seen below. Inserting (3·11), (3·13), (3·14), (3·15) and (3·16) into (3·8), we have the Hamiltonian expressed in new co-ordinates:

$$\begin{aligned} H= & -\varepsilon_p-\varepsilon_s \\ & +\boldsymbol{P}^2/2m_c+1/\kappa_0\cdot V(\boldsymbol{R}) \\ & +\varepsilon\sum B_w^* B_w \\ & +\frac{e\gamma\hbar^2}{m\sqrt{L^3}}\sum_w \frac{1}{\left(\varepsilon+\dfrac{\hbar^2 w^2}{2m}\right)^2}\frac{\boldsymbol{w}}{\boldsymbol{w}}\cdot\text{grad } V(\boldsymbol{R})\,\{B_w \exp(i\boldsymbol{w}\cdot\boldsymbol{R}) \\ & \qquad +B_w^* \exp(-i\boldsymbol{w}\cdot\boldsymbol{R})\}, \end{aligned} \tag{3·17}$$

where

$$-\varepsilon_s=-\alpha\varepsilon \tag{3·18}$$

means the self-energy of the electron e due to the electronic polarization around itself, and m_c is the effective mass of the conduction electron in which the interaction with the electronic polarization is already taken into account, and is given by

$$\frac{1}{m_c}=\frac{1}{m}\left(1-\frac{\alpha}{6}\right). \tag{3·19}$$

Thus we see that the bottom of the conduction band is lowered by $\alpha\varepsilon$ from that which is obtained if we do not take account of the interaction, while the effective mass of the band is given by m_c instead of m. As the interaction constant α is 0.5~1 for real crystals, the self-energy turns out to be pretty large, but because of the overestimation caused by the continuum approximation, the above value should be reduced to about half of it. On the other hand, the correction $\alpha/6$ of the effective mass is of less importance.

The equation (3·17) is interpreted as follows. As a result of clothing the fixed charge $\rho(\boldsymbol{r})$ and the moving electron e with electronic polarization, there appear in the first line two kinds of self-energy, and these dressed units interact with each other, so that the potential $V(\boldsymbol{R})$ is shielded by a factor $1/\kappa_0$, leading to the classical description as is seen in the second line. Of course, $\boldsymbol{P}$ and $\boldsymbol{R}$ should be interpreted as the momentum and the position of the electronic polaron rather than as those of the electron itself. The third line corresponds to the free excitons, which could exist independently of the motion of the electronic polaron, but for the last term. The last term which is interpreted as the Hamiltonian for the interaction corresponds to the production and annihilation of excitons in the neighbourhood of the imperfection Q by exchanging energy with the electronic polaron.

If we consider a trapped state of the electronic polaron as a stationary state problem, the interaction term causes the production of virtual excitons in addition to those which always accompany a free electronic polaron. As a result the energy of trapping is deeper than the value which would be obtained from the Hamiltonian

$$\boldsymbol{P}^2/2m_c+1/\kappa_0\cdot V(\boldsymbol{R}).$$

This is analogous to the Lamb-shift problem[17] in the hydrogen atom, if we replace the electronic polarization field in a crystal by the radiation field in vacuum. But in our case the Hamiltonian (3·17) is only an approximate expression, so that this problem belongs to the interest of rather academic nature. Far more interesting and important application of (3·17) is the calculation of the transition probability for the processes in which free excitons are produced or destroyed in the neighbourhood of the imperfection. We shall now turn to one of such problems.

§ 4. Ionization of a trapped electron by an exciton

Recently Apker and Taft[10)11] carried out a series of very interesting and excellent experiments on the external photoelectric effects in alkali-halides. They observed an enhanced effect of photoelectric yield in the wave-length region of irradiation which corresponds to the first exciton absorption band of the crystal. They concluded that this effect is due to the ionization of F-center electrons by excitons.

On the other hand, it has been generally considered to be somewhat curious that no one has observed the emission due to exciton annihilation. From this reason Seitz[12] infers that the excitons annihilate by giving its energy to some kind of imperfection under the ordinary conditions of purity.

Under these circumstances it is highly necessary and interesting to calculate the transition probability for the ionization process of a trapped electron by an exciton.

If we assume that the trapping potential $V(\boldsymbol{R})$ is caused by a point charge ze located at the origin, the Hamiltonian (3·17) is written as follows:

$$H=H_0+H', \tag{4·1}$$

$$H_0=\boldsymbol{P}^2/2m-1/\kappa_0\cdot ze^2/R+\varepsilon\sum B_w^*B_w, \tag{4·2}$$

$$H'=\frac{e\gamma\hbar^2}{m\sqrt{L^3}}\sum_w\frac{1}{\left(\varepsilon+\dfrac{\hbar^2w^2}{2m}\right)^2}\frac{\boldsymbol{w}}{w}\cdot\mathrm{grad}\left(-\frac{ze^2}{R}\right)\{B_w\exp(i\boldsymbol{w}\cdot\boldsymbol{R})+B_w^*\exp(-i\boldsymbol{w}\cdot\boldsymbol{R})\}, \tag{4·3}$$

where we have replaced m_c in (3·17) by m, because the difference between them is rather small. We consider the following two eigenstates of (4·2) between which transition occurs owing to the perturbation (4·3).

(i) *Initial state*

excitons : $N_w=B_w^*B_w=1$, $N_{w'}=0$ for all other $\boldsymbol{w}'$.

electron : $1s$-state in a Coulomb field,

$$-\mathcal{E}_t=-m_0/m\cdot z'^2\mathcal{E}_H, \tag{4·4}$$

$$\psi_t=\left(\frac{z'}{a_H}\right)^{3/2}\frac{1}{\sqrt{\pi}}\exp\left(-\frac{z'}{a_H}R\right), \tag{4·5}$$

where m_0 is the electron mass, a_H the Bohr radius and $\mathcal{E}_H=13.5$ ev the energy of the hydrogen $1s$-state. z' is defined by

$$z'=z/\kappa_0\cdot m/m_0. \tag{4·6}$$

The energy of the initial state is given by

$$E_0^i=\mathcal{E}-\mathcal{E}_t=\mathcal{E}(1-\Delta), \qquad \Delta=\mathcal{E}_t/\mathcal{E}. \tag{4·7}$$

(ii) *Final state*

excitons : $N_w=0$ for all $\boldsymbol{w}$'s.

electron : ionized state in a Coulomb field with asymptotic wave number $\boldsymbol{k}$,[18]

$$\psi_k(\boldsymbol{R})=\frac{1}{\sqrt{L^3}}\exp(i\boldsymbol{k}\cdot\boldsymbol{R})\,\Gamma(1-ip)\exp\left(\frac{1}{2}p\pi\right)F(ip,\,1,\,ikR(1-\cos\theta')) \tag{4·8}$$

$$=\frac{1}{\sqrt{L^3}}\exp\left(\frac{1}{2}p\pi\right)\sum_{l=0}^{\infty}\frac{\Gamma(l+1-ip)}{(2l)!}(2ikR)^l\exp(ikR)$$

$$\times F(l+1-ip,\,2l+2,\,-2ikR)\,P_l(\cos\theta'), \tag{4·8'}$$

where F means a confluent hypergeometric function, and the parameter p is defined by

$$p=z'/a_Hk. \tag{4·9}$$

Energy conservation requires that

$$E_0^f=\hbar^2k^2/2m=E_0^i=\mathcal{E}(1-\Delta), \tag{4·10}$$

from which we have, by (4·9), the relation

$$p^2=\Delta/(1-\Delta). \tag{4·11}$$

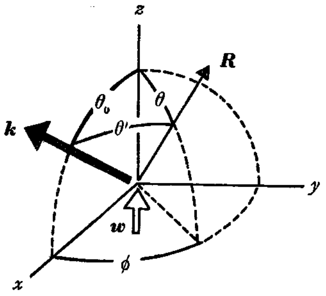

Fig. 1.

Let us now calculate the transition probability. We use the co-ordinates illustrated in Fig. 1 : the incident direction of the exciton ($\|\boldsymbol{w}$) is taken as z-axis, and x-axis is chosen so that the wave vector k of the ionized electron lies in the xz-plane. The polar co-ordinates referred to these axes are denoted by (R,θ,ϕ), and the angles $\widehat{\boldsymbol{kz}}$ and $\widehat{\boldsymbol{kR}}$ are written θ_0 and θ', respectively.

According to the time-dependent perturbation theory, the transition probability for the electron to be emitted in the direction θ_0 within a solid angle $d\Omega_0$ is given by

$$W(\theta_0)\,d\Omega_0=\frac{2\pi}{\hbar}|H'_{if}|^2\frac{1}{4\pi}\rho(E)\,d\Omega_0$$

$$=\frac{mkL^3}{(2\pi)^2\hbar^3}|H'_{if}|^2 d\Omega_0, \tag{4·12}$$

where $\rho(E)$ is the state density of a free electronic polaron with energy E. The matrix element H'_{if} can be written as

$$H'_{if}=\frac{ze^3\gamma\hbar^2}{m\sqrt{L^3}}\frac{1}{\left(\mathcal{E}+\dfrac{\hbar^2w^2}{2m}\right)^2}\int\psi_t^*\frac{\cos\theta}{R^2}\exp(-i\boldsymbol{w}\cdot\boldsymbol{R})\,\psi_k d\boldsymbol{R} \tag{4·13}$$

by using (2·12) and (4·3). Putting (4·5) and (4·8′) into the integral, then making use of addition formulae for Legendre polynomials to express $P_l(\cos\theta')$ in terms of θ, θ_0 and ϕ, finally integrating term by term, one finds the following double series for the matrix element :

$$H'_{if}=\frac{1}{L^3}\frac{2i\pi e^3\gamma\hbar^2 zz'^{3/2}}{m{a_H}^{3/2}}\frac{\exp(\frac{1}{2}p\pi)}{k\left(\mathcal{E}+\dfrac{\hbar^2w^2}{2m}\right)^2}$$

$$\times\sum_{l=0}^{\infty}\sum_{m=0}^{\infty}\frac{\Gamma(l+1-ip)}{(2l)!}P_l(\cos\theta_0)\frac{1}{2^{2m}}\frac{(-1)^m(l+2m)\,(2l+2m-1)\,!}{m\,!\,\Gamma(l+m+\frac{3}{2})}$$

$$\times\frac{\lambda^{l+2m-1}}{(p-i)^{2l+2m}}F\left(l+1-ip,\,2l+2m,\,2l+2,\,\frac{-2i}{p-i}\right) \tag{4·13′}$$

where λ is defined by

$$\lambda=w/k, \tag{4·14}$$

and F is the hypergeometric function of customary use.

The total probability for the process is obtained by integrating (4·12) over all directions after inserting (4·13′) into (4·12) :

$$W_T(p,\lambda)=\int W(\theta_0)\,d\Omega_0$$

$$=\frac{32\pi^2}{L^3}\frac{\hbar e^2}{m\mathcal{E}}{\kappa_0}^2\left(1-\frac{1}{\kappa_0}\right)\frac{p^5(1+p^2)^2\exp(p\pi)}{(1+p^2+\lambda^2)^4}S(p,\lambda), \tag{4·15}$$

where $S(p,\lambda)$ is given by

$$S(p,\lambda)=\sum_{l=0}^{\infty}\frac{|\Gamma(l+1-ip)|^2}{\{(2l)!\}^2(2l+1)}\frac{\lambda^{2l-2}}{(1+p^2)^{2l}}$$

$$\times\left|\sum_{m=0}^{\infty}\frac{(l+2m)\,(2l+2m-1)\,!}{m\,!\,\Gamma(l+m+\frac{3}{2})}\left\{\frac{i}{p-i}\frac{\lambda}{2}\right\}^{2m}\right.$$

$$\left.\times F\left(l+1-ip,\,2l+2m,\,2l+2,\,\frac{-2i}{p-i}\right)\right|^2. \tag{4·16}$$

We have carried out the calculation of this series to the fourth power in λ, by making use of the equation for the Γ-function:

$$|\Gamma(1-ip)|^2 \exp(p\pi)=\frac{2p\pi}{1-\exp(-2p\pi)} \qquad (4\cdot17)$$

and the explicit forms of the hypergeometric functions F which are given in the Appendix II. If we use (4·14), (4·9) and (3·12) to rewrite the result in terms of p and w, the total probability W_T can be expressed as follows:

$$W_T(p,\,w)=\frac{1}{L^3}\frac{\hbar e^2}{m\mathcal{E}}\kappa_0^2\left(1-\frac{1}{\kappa_0}\right)G(p,\,w), \qquad (4\cdot18)$$

where

$$G(p,\,w)=g_0(p)/\{1+(w/u)^2\}^4\cdot\{1+g_1(p)\,(w/u)^2+g_2(p)\,(w/u)^4+\cdots\}, \qquad (4\cdot19)$$

and

$$g_0(p)=\frac{256\pi^2}{3}\frac{p^6\exp(-4p\cot^{-1}p)}{\{1-\exp(-2p\pi)\}\,(p^2+1)^3} \qquad (4\cdot20)$$

$$\begin{aligned} g_1(p)=\frac{1}{5(p^2+1)\,(p^2+4)}\{&(172p^4+147p^2+23)\\ &-2(p^2+1)\,(23p^2+11)\exp(2p\cot^{-1}p)\\ &+3(p^2+1)^2\exp(4p\cot^{-1}p)\}, \end{aligned} \qquad (4\cdot21)$$

$$\begin{aligned} g_2(p)=\frac{1}{35(p^2+1)\,(p^2+4)\,(p^2+9)}\{&(29517p^6+49646p^4+22385p^2+3312)\\ &-8(p^2+1)\,(997p^4+1324p^2+279)\exp(2p\cot^{-1}p)\\ &+540(p^2+1)^3\exp(4p\cot^{-1}p)\}. \end{aligned} \qquad (4\cdot22)$$

For all values of p between 0 and ∞ (corresponding to $0\leqq\mathcal{E}_t\leqq\mathcal{E}$), $g_1(p)$ and $g_2(p)$ are comparatively small and w-dependence of $G(p,\,w)$ is mainly determined by the factor

$$1/\{1+(w/u)^2\}^4,$$

so that we can conclude that excitons with small wave-number w are the most effective in ionizing a trapped electron. For the same reason, p-dependence of $G(p,w)$ is mainly determined by $g_0(p)$ so far as w is small compared with u. The curve (a) of Fig. 2 shows $g_0(p)$ as a function of $\varDelta=\mathcal{E}_t/\mathcal{E}$ through the relation (4·11). Thus the ionization probability tends to a finite value as the trapping energy becomes nearer to the exciton energy, in spite of the fact that

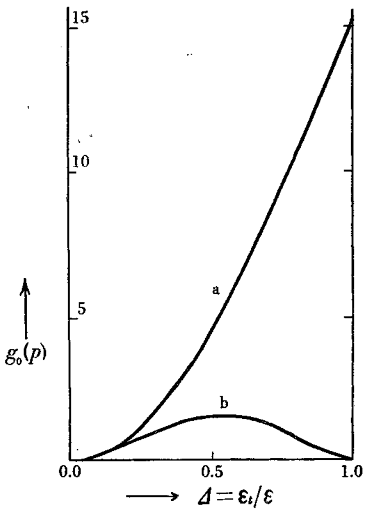

Fig. 2.

the state density of final states of the ionized electron tends to zero in this limit. This is due the property of the wave function (4·8), the amplitude of which at the origin tends to infinity as k approaches zero. In fact, when we use plane wave approximation instead of the strict wave function (4·8), we obtain the curve (b), which coincides with the curve (a) for small values of Δ but deviates from it for larger values, and tends to zero as Δ approaches unity.

§ 5. Application to real crystals

Before we apply the result obtained in the preceding section to real crystals, we must correct them because we have been assuming a very simple model according to which the excited states of crystal electrons consist of only one exciton band. In real crystals, such as alkali-halides, however, the optical absorption measurements in the fundamental region show that the excited states consist of a few number of exciton bands together with an ionization continuum. This means that the relation (2·18) between γ and κ_0 has to be replaced by a generalized one (which is nothing but a dispersion formula for zero frequency) :

$$\sum_i \gamma_i^2/\mathcal{E}_i = 2\pi(1-1/\kappa_0) \tag{5·1}$$

in which γ_i and $\mathcal{E}_i$ are the values for each exciton bands and an ionization continuum. Thus the contribution γ_i^2 of a single (for example, the first) exciton band is much smaller than the value γ^2 given by (2·18). Since the perturbation term H' in (4·3) is proportional to γ, we must correct the result (4·18) for the transition probability by multiplying a factor γ_i^2/γ^2. Now each γ_i is connected with the oscillator strength f_i of the corresponding exciton absorption through the equation (2·11) and the relation between the dipole moment μ_i and the oscillator strength :

$$f_i = 2m_0\mathcal{E}/3\hbar^2 \cdot \mu_i^2 , \tag{5·2}$$

leading to the correction factor :

$$\frac{\gamma_i^2}{\gamma^2} = \frac{12\pi e^2\hbar^2}{m_0\mathcal{E}^2 v_0(1-1/\kappa_0)} f_i . \tag{5·3}$$

In the following we shall drop the suffix i of f, confining ourselves to the *first* exciton band.

Assuming the density of trapped electrons to be n_t/c.c., the probability for a longitudinal exciton with wave number w to annihilate by ionizing any of the trapped electrons is now given by

$$W_I = \frac{12\pi\hbar^3 e^4 \kappa_0{}^2}{m_0{}^2\mathcal{E}^3 v_0} n_t G(p, w) f \tag{5·4}$$

where we have replaced m by m_0. In case of alkali-halides with lattice constant a, v_0 is equal to $2a^3$, therefore (5·4) is rewritten as

$$W_I = 1.0 \times 10^{-6} \times \kappa_0{}^2 (\mathcal{E}_H/\mathcal{E})^3 (a_H/a)^3 n_t G(p, w) f \,\mathrm{sec}^{-1} . \tag{5·4'}$$

Without the knowledge on the f-value, we can compare (5·4′) with the probability $W_E^{(20)}$ for the annihilation of an exciton through spontaneous emission which is also proportional to f:*

$$W_E = 8 \times 10^9 (\mathcal{E}/\mathcal{E}_H)^2 f \sec^{-1}. \tag{5·5}$$

Of these two ways of destruction of excitons, the ionization occurs only for longitudinal waves, while the radiation process is possible only for transverse waves. If we neglect the energy difference between the two kinds of waves, the ratio of their probable numbers is 1/3 : 2/3. The factor 2/3 is already taken into account in (5·5). In order that the ionization process is more probable than the emission, the following condition must be satisfied :

$$W_I/3 > W_E. \tag{5·6}$$

As an example for numerical estimation we take the case of KI crystal containing F-centers, with which Apker and Taft[10)] carried out one of their experiments. Inserting the values

$\mathcal{E} = 5·6$ eV,

$\mathcal{E}_t = 2$eV (presumed from the F-absorption energy 1.7 eV)

$a = 3.53$ Å, $\kappa_0 = 2,7$

into (5·4′) and (5·5), and assuming that $w \doteqdot 0$, we have

$$W_I = 0.8 \times 10^{-6} n_t f \sec^{-1}., \tag{5·7}$$

$$W_E = 1.4 \times 10^9 f \sec^{-1}.,$$

the condition (5·6) therefore means that

$$n_t > 0.5 \times 10^{16}/\text{c.c.}. \tag{5·8}$$

Thus we can safely conclude that for all alkali-halide crystals, excitons annihilate rather by ionizing F-electrons than by spontaneous emission, if the density of F-centers is larger than 10^{16}/c.c..

Apker and Taft[10)] presume that about 10^{19}/c.c. F-centers are formed in their experiment on KI ; in case of such a large density, the ionization of F-centers is predominant according to the above discussion, thus our calculation supports their interpretation of exciton-enhanced photoemission as being caused by the F-electron ionization.

More generally we can conclude that excitons annihilate mainly by ionizing electrons trapped in various impurity levels under the usual condition of purity. (Deeper traps are more efficient in destroying excitons as is seen from the curve (a) of Fig. 3.) This is

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* The optical properties of the system which is described by means of exciton waves are approximately the same as those of a system consisting of free atoms.[19)] This rule can be applied to the case of the spontaneous emission of an exciton, the probability being given by that of a free atom.[12)]

qualitatively in agreement with Seitz's[12] speculation on the mechanism of exciton destruction, according to which the impurity content of the order of 10^{-7} is sufficient to suppress spontaneous emission of excitons. It would be very interesting if the relation between the density of impurities and the photoconductivity in the first exciton absorption region were investigated experimentally, though it would be somewhat difficult owing to the formation[10] of color-centers during irradiation.

In the above discussion we have tacitly assumed that the exciton band has a positive effective mass so that only the excitons with wave number $w \doteqdot 0$ prevail in thermal equilibrium. If the effective mass is negative, such excitons will decrease through scattering by lattice vibrations more rapidly than they annihilate in any way, so that the emission process (which is possible only for $w \doteqdot 0$) will be less probable and the condition (5·8) has to be replaced by even more lenient one.

In order to estimate W_I absolutely instead of in comparison with W_E, it is necessary to know the value of f. Dexter[21] recently carried out theoretical calculation and obtained the value $f=0.07$ for NaCl. On the other hand it is difficult to estimate the f-value from experimental data; perhaps it would be safe to assume that f is of the order of 0.05 for the first exciton bands in all alkali-halides, on the grounds of (*a*) absorption data[22],[10–11], (*b*) relation to the β-bands[23] and (*c*) Mayer's analysis[24] of dispersion data.* Assuming this value for the first exciton band of KI, and $n_t=10^{19}$/c.c. for the density of F-centers, the largest value experimentally obtainable, we have, by (5·7),

$$W_I/3 \sim 10^{11}\ \mathrm{sec}^{-1}. \qquad (5\cdot 7')$$

This is still much smaller than the frequency of scattering of excitons by lattice vibrations, which is estimated to be of the order of

$$W_V = 10^{12} \sim 10^{13}\ \mathrm{sec}^{-1}. \qquad (5\cdot 9)$$

As was stated in § 2, only the longitudinal excitons are effective in ionizing trapped electrons, while the excitons which are produced by irradiation as in Apker and Taft's experiments are of transverse type. By comparison of (5·9) and (5·7′), however, we see that the equilibrium number of longitudinal waves are produced by scattering in sufficiently short time; thus our estimation remains correct just the same.

Another point which should be discussed is the energy difference between the longitudinal and the transverse waves, which has been neglected in the above estimation. Heller and Marcus[14] recently noticed that even without overlapping of atomic orbitals an exciton band has a finite breadth due to the dipole-dipole interaction of atoms which are excited one after another, and that the longitudinal waves have higher energies than the transverse ones. But in real crystals most of the contribution to the total oscillator strength for the excitation of crystal electrons comes from the transitions to higher states than the

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* In estimating the f-value from the data (*a*) and (*b*), we have used Smakula's formula[25] which seems to the author to be approximately valid also for the first exciton band, because the most part of the characteristic absorption lies in the shorter wave-length region.

first exciton band, so that the dipole-dipole interaction stated above is shielded by a factor $1/\kappa_0$, thus leading to a rather small value of the separation energy. Moreover the influence of overlapping would complicate the situation. Therefore their results does not seem to affect our estimation so seriously.

In conclusion the author wishes to express his sincere thanks to Professor T. Muto, Professor T. Inui and Professor F. Seitz for their valuable suggestions and discussions. His thanks are also to Mr. Y. Uemura and Mr. H. Miyazawa for their continual encouragements and stimulations to this problem. This work is indebted to the Scientific Research Expenditure of the Ministry of Education.

Appendix I. Proof of the equation (2·18)

Equation (2·18) can be proved in the same way as Fröhlich, Pelzer and Zienau[1] did in the lattice polaron problem. That is, we consider a classical point charge e_1 fixed at $\boldsymbol{r}=0$. Then the energy of the system composed of e_1 and the crystal C is written, by (2·14) and (2·16), as

$$H_1=\varepsilon\sum_{w} b_w^* b_w+\frac{e_1\gamma}{\sqrt{L^3}}\sum_{w}\frac{i}{w}(b_w-b_w^*).$$

The minimum of this expression is realized for the values of b_w:

$$\overline{b_w}=\frac{e_1\gamma}{\varepsilon\sqrt{L^3}}\frac{i}{w}.$$

This electronic polarization causes the potential

$$\overline{\varphi_1(\boldsymbol{r})}=\frac{\gamma}{\sqrt{L^3}}\sum_{w}\frac{i}{w}\{\overline{b_w}\exp(i\boldsymbol{w}\cdot\boldsymbol{r})-\overline{b_w^*}\exp(-i\boldsymbol{w}\cdot\boldsymbol{r})\}=-\frac{\gamma^2}{2\pi\varepsilon}\frac{e_1}{r}$$

according to (2·14). In order that this be equal to

$$-(1-1/\kappa_0)\cdot e_1/r$$

as is required by electrostatics, the relation (2·18) has to be satisfied.

Appendix II. Explicit forms of the hypergeometric functions used in the calculation

The hypergeometric functions appearing an (4·16) are such that the two parameters $\beta=2l+2m$ and $\gamma=2l+2$ are integers. We can, therefore, express them in terms of elementary functions as follows.

Starting out from the relation

$$F(\alpha,\beta,\beta,z)=(1-z)^{-\alpha}$$

which corresponds, in our case, to $m=1$, we can utilize the step-up recurrence formula[26] for the hypergeometric functions

$$zF'(\alpha,\beta,\gamma\,;z)+\beta F(\alpha,\beta,\gamma\,;z)=\beta F(\alpha,\beta+1,\gamma\,;z)$$

repeatedly in order to obtain the expressions for the cases $m>1$. Thus we have, for example,

$$F\left(l+1-ip,\ 2l+2,\ 2l+2,\ \frac{-2i}{p-i}\right)=\left(\frac{p-i}{p+i}\right)^{l+1}\exp\left(-2p\cot^{-1}p\right)$$

$$F\left(l+1-ip,\ 2l+4,\ 2l+2,\ \frac{-2i}{p-i}\right)$$
$$=\frac{(2l-1)p^2-1}{2l+3}\,\frac{(p-i)^{l+1}}{(p+i)^{l+3}}\exp\left(-2p\cot^{-1}p\right).$$

When $m=0$, it is more convenient to make use of the expressions in infinite series: we can write, for example,

$$F(\alpha,2,4\,;z)=\sum_{n=0}^{\infty}\frac{\alpha(\alpha+1)\cdots(\alpha+n-1)\cdot 2\cdot 3}{n!\,(n+2)\,(n+3)}z^n$$
$$=\frac{6}{(\alpha-1)\,(\alpha-2)\,(\alpha-3)}\frac{d}{dz}\left\{\frac{(1-z)^{-(\alpha-3)}}{z^2}-\frac{1}{z^2}-\frac{\alpha-3}{z}\right\}.$$

The results up to the case $l=3$ are as follows:

$$F\left(2-ip,\ 2,\ 4\,;\ \frac{-2i}{p-i}\right)=3\frac{p-i}{p+i}\exp\left(-2p\cot^{-1}p\right),$$

$$F\left(3-ip,\ 4,\ 6\,;\ \frac{-2i}{p-i}\right)=\frac{5}{2}\left(\frac{p-i}{p+i}\right)^2\frac{1}{p^2+4}\left\{(23p^2+11)\exp\left(-2p\cot^{-1}p\right)\right.$$
$$\left.-3\,(p^2+1)\right\},$$

$$F\left(4-ip,\ 6,\ 8\,;\ \frac{-2i}{p-i}\right)=\frac{63}{2}\frac{(p-i)^4}{(p+i)^2}\frac{1}{(p^2+4)\,(p^2+9)}$$
$$\times\left\{(37p^2+13)\exp\left(-2p\cot^{-1}p\right)-5\,(p^2+1)\right\}.$$

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Note added in proof: The estimation (5·8) for the critical density of F-centers is in qualitative agreement with that of the previous work by Dexter and Heller[27] who considered the F-electron ionization by an exciton to take place through two stages, whereas our formulation permits direct process. Though both are based on somewhat different points of view, they are in accordance as regards the most essential point, that is, the transition dipole field of the exciton is responsible for the process. The author wishes to thank Dr. Dexter for informing his interesting idea about this problem.[28]