$$H_0 = -2^{7/3} C Z_1^{7/3}/\lambda = -5.04 C Z_1^{7/3}/\lambda.$$

Thus

$$\frac{H - H_0}{H_0} = 4.17\%, \quad \frac{H_0 - H_1}{H_0} = 1.38\%,$$

$$\frac{{}^1\!/_2 (H + H_1) - H_0}{H_0} = 1.38\%.$$

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[1] P. Gombas, *Statistical Theory of the Atom and its Applications,* (Russian translation of *Statistische Theorie des Atoms und Ihre Anwendungen,* Springer-Verlag, Vienna, 1949).IIL, Moscow, 1951.

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On the Exciton Mechanism for Capture of Current Carriers in Homopolar Semiconductors

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Capture of charge carriers by structural defects, in which energy is transferred to small radius excitons, is investigated. The temperature dependence of recombination coefficients is determined.

1. INTRODUCTION

THE PROBLEM OF THE MECHANISM for capture of current carriers by impurity centers is still unsolved. This statement is particularly applicable to the mechanism for carrying off the energy which is liberated during the localization of a carrier which makes a transition from a band to an impurity level. Until recently it was implicitly assumed that this energy is given directly to the lattice, which undergoes a deformation during an electron transition of this type. Only recently it has been shown[1–4] that this possibility is by no means the only one, and that the so-called radiationless transitions can (at least, in their first stage) also proceed without participation by the lattice, but rather via a redistribution of the energy within the many-electron system itself. In Refs. 1 – 3 this redistribution was caused by the presence of another carrier, to which the liberated energy was transferred. Reference 4 pointed out that for a radiationless transition it is sufficient for the energy to be transferred to any neutral excitation of the many-electron system, and treated the process of capture with excitation of plasma oscillations. In all these cases, the conversion of the excitation energy into heat (*i.e.*, conversion into phonons) occurs only in a later, much slower stage of the process.

In the present paper we shall treat the "exciton" mechanism for capture, in which the liberated energy goes into the formation of "Frenkel excitons" (*i.e.*, excitons of small radius and, consequently, rather high dissociation energy). The inverse process – the ionization of impurity centers by exciton impact – was discussed earlier by Lashkarev[5] and Zhuze and Ryvkin,[6] and treated quantitatively by Toyozawa[7] (*cf.* also Ref. 18). However, there are various contradictory points in Ref. 7. In the first place, in the formulation of the problem given there, the interaction of the electrons with the exciton field is not at all small, whereas a weak coupling method is used in the calculation. In addition, even if we disregard this main objection, the specific computations in Ref. 7 are applicable only to traps which are sufficiently shallow to be described by the "hydrogen" model. All of these considerations have compelled us once again to consider the exciton mechanism for capture, using for this purpose the consistent many-electron theory of semiconductors developed earlier.[8] In accordance with many well known experimental results, we shall consider the capture of current carriers by deep traps. Calculation of the absolute value of the capture cross section turns out to be extremely difficult; however, its temperature dependence can be determined quite well, as we shall show later.

In order to emphasize the essentially "intra-electronic" character of this phenomenon, we shall treat the problem without including the interaction of excitons with the lattice. As is well known,[9–10] inclusion of the interaction with the lattice gives rise to important features of the exciton spectrum; however, the interaction of the electrons with one another still plays the major role in the process in which we are interested.

2. INITIAL EQUATIONS

As shown in Ref. 8, on the basis of the general theory of excitations in many-electron systems developed in Ref. 11, the wave functions of excited states of a homopolar semiconductor can be represented as*

$$\psi_m = L_m \psi_0, \tag{2.1}$$

$$L_m = \sum_{\alpha_1,\ldots,\alpha_m} \sum_{\beta_1,\ldots,\beta_m} \varphi_m(\alpha_1,\ldots,\alpha_m, \beta_m,\ldots,\beta_1)\, a^*_{\alpha_1}\ldots a^*_{\alpha_m} a_{\beta_m}\ldots a_{\beta_1}, \tag{2.2}$$

where a^*_α, a_β are the Fermi operators for creation and annihilation of particles in states α and β; ψ_0 is the wave function of the ground state of the system, for which (by definition) the occupation numbers are $N(\beta) = 1$, $N(\alpha) = 0$. The index α denotes the set of quantities g, a, s, which give respectively the number of the elementary cell, the number of the atom in the cell, and the atomic quantum numbers,† and the spin quantum number. Similarly, $\beta = \{\mathrm{f}, b, t\}$, where f, b, t have the same significance as g, a, s, respectively. The function φ_m is the wave function of a system with m pairs of elementary excitations; for states of low excitation (for which m is small compared to the total number of atoms in the lattice) it can be written as a determinant of the functions φ_1 referring to the various energy values λ_1. The functions are given by the equations

$$\sum_{\alpha'}\Big\{A(\alpha;\alpha') + 2\sum_{\beta''} B(\alpha,\beta'';\beta'',\alpha')\Big\}\varphi_1(\alpha';\beta)$$
$$-\sum_{\beta'}\Big\{A(\beta';\beta) + 2\sum_{\beta''} B(\beta',\beta'';\beta'';\beta)\Big\}\varphi_1(\alpha;\beta')$$
$$-2\sum_{\alpha',\beta'} B(\alpha,\beta';\beta,\alpha')\varphi_1(\alpha';\beta') = \lambda_1\varphi_1(\alpha;\beta). \tag{2.3}$$

A and B are the matrix elements of the additive and binary parts of the Hamiltonian, respectively, calculated with the system of orthogonalized "quasi-atomic" functions ψ_α, ψ_β; the quantity $B(\alpha_1, \alpha_2; \beta_2, \beta_1)$ is antisymmetric in the indices α_1 and α_2, β_2 and β_1. In Ref. 8 it was shown that Eq. (2.3) has solutions which describe excess electrons and holes which behave qualitatively like the "non-interacting electrons" of the standard band theory (hereinafter we shall for brevity simply talk of electrons).. As shown in Ref. 11, this formulation of the problem is approximate, and valid only if the quantities $B(\alpha_1, \alpha_2; \alpha, \beta)$, $B(\alpha, \beta; \beta_1, \beta_2)$ are small compared with the other matrix elements of the Hamiltonian. Matrix elements of the type indicated connect states with different values of m, so that they give rise to creation and annihilation of elementary excitations and in particular to recombination of excess electrons and holes. If we treat quantities of the type of $B(\alpha, \beta; \beta_1, \beta_2)$ as small perturbations, it is easy to get the corresponding transition probabilities. In the first approximation only transitions with unit change of m are possible. In particular, the transition probability (per unit time) from $m = 1$ to $m = 2$ is

$$P(1\to 2) = (2\pi/\hbar)\,|H_{21}|^2\,\delta(\lambda_2 - \lambda_1), \tag{2.4}$$

where (remembering that the ground state energy of the system is taken to be zero),

$$H_{21} = 2\sum_{\alpha_1,\alpha_2}\sum_{\beta_1,\beta_2}\bar{\varphi}_2(\alpha_1,\alpha_2;\beta_2,\beta_1)$$
$$\times\Big\{\sum_{\alpha}[\varphi_1(\alpha;\beta_1)B(\alpha_1,\alpha_2;\beta_2,\alpha)]$$
$$-\varphi_1(\alpha;\beta_2)B(\alpha_1,\alpha_2;\beta_1,\alpha)] \tag{2.5}$$
$$+\sum_{\beta}[\varphi_1(\alpha_2;\beta)B(\beta,\alpha_1;\beta_2,\beta_1)$$
$$-\varphi_1(\alpha_1;\beta)B(\beta,\alpha_2;\beta_2,\beta_1)]\Big\}.$$

For compactness, we have omitted the "quantum

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* For the conditions of applicability of this representation of the wave functions of excited states, *cf.* Ref. 11.

† Unlike Ref. 8, in the present paper we take account of all the excited atomic states; *i.e.*, the system of basic functions which is used in making the transition to the second-quantized representation is complete.

numbers" characterizing the functions φ_1 and φ_2. The functions φ_1 and φ_2 must be normalized as follows:

$$\sum_{\alpha,\ \beta} |\varphi_1(\alpha;\ \beta)|^2 = 1, \tag{2.6}$$

$$4 \sum_{\alpha_1,\ \alpha_2} \sum_{\beta_1,\ \beta_2} |\varphi_2(\alpha_1,\ \alpha_2;\ \beta_2,\ \beta_1)|^2 = 1. \tag{2.7}$$

We note that the calculation of the transition probability is of interest not only for the problem of recombination of current carriers, but also for estimating the degree of applicability of the method; it is clear that the method is applicable only if the lifetime of a current carrier is large compared to other characteristic times which describe the behavior of the electron system. Actually this is the case.

3. UNPERTURBED PROBLEM. EXCITONS OF SMALL RADIUS

We first consider the unperturbed problem (2.3). As shown in Ref. 8, Eq. (2.3) has two types of solution describing, respectively, a free electron and a hole, and an exciton. The solutions of the first type were investigated in general in Ref. 8. Neglecting the interaction between the free electron and hole, they have the form

$$\varphi_1(\alpha;\ \beta) = \varphi_n(\alpha)\,\varphi_p(\beta),\ \lambda_1 = \lambda_n + \lambda_p \tag{3.1}$$

(the indices n and p refer to electron and hole), where

$$\begin{aligned} \varphi_n(\alpha) &= \chi_n^{k,\ \mu}(a)\,S_\sigma(s)\,F_n^k(\mathbf{g}), \\ \varphi_p(\beta) &= \chi_p^{l,\ \nu}(b)\,S_\tau(t)\,F_p^l(\mathbf{f}). \end{aligned} \tag{3.2}$$

Here **k**, **l** are the quasi-momenta of electron and hole, σ and τ indices giving their spins, μ and ν various discrete quantum numbers (*e.g.*, the band number, *etc.*). The functions F_n and F_p are plane waves in the ideal lattice; in a non-ideal lattice they are wave functions in either the continuous or discrete spectrum for a quasi-particle moving in the field of the structural defect. (In this case the quasi-momenta **k** or **l** do not occur.) In the case of deep traps (located in the middle of a forbidden band) the functions of the discrete spectrum fall off very rapidly with distance from the trap. It is easy to see that the only important values of the quasi-momenta are those close to zero (if they are measured from the points corresponding to minima on the surfaces of constant energy). Actually, **k** and **l** enter into (3.2) and (2.5) either through the energies λ_n and λ_p, or in the combinations $ka/\hbar$, $la/\hbar$, where a is a characteristic length which determines the rate at which the "localized" function F falls off. Also essential here is the usual assumption that exchange integrals containing quasi-atomic functions referring to different centers fall off rapidly. Upon averaging over the equilibrium distribution we get quantities of order

$$a/L \ll 1,\ kT/J \ll 1, \tag{3.3}$$

where L is the "thermal" wavelength of the current carrier, J is the ionization energy of the deep trap (*i.e.*, the difference between the energy of the system when the carrier is at the bottom of the corresponding band and when it is in the trapping level). The inequalities (3.3) comprise the basic approximation used in the present paper. Wherever possible, the quantities which appear on the left in (3.3) will be set equal to zero.

We now turn to exciton-type solutions of (2.3). A complete investigation of these solutions is hardly meaningful at present, since we cannot say too much about the coefficients in (2.3) without making crude assumptions about models. However, for our purposes it is sufficient merely to establish the fact that excitons of small radius (of the order of the lattice constant) exist. To do this, we limit the class of functions $\varphi_1(\alpha;\ \beta)$ by the condition $\varphi_1(\alpha;\ \beta) \sim \Delta(\mathbf{g} - \mathbf{f})$ (Δ is the delta function). Then Eq. (2.3) describes the joint motion of the electron and the hole (*i.e.*, the motion of the exciton), and the dissociation energy of the exciton is greater (*i.e.*, the energy of the system is less) than on the hydrogen model. Since Eq. (2.3) was gotten from a variational principle, the true minimum of the energy, which would be obtained if we did not limit the class of functions φ_1 by the auxiliary condition given above, lies even lower, and the functions corresponding to it also decrease rapidly with increasing $|\mathbf{g} - \mathbf{f}|$ (because all "smooth" functions are described by the hydrogen model of the exciton). Thus (2.3) has exciton solutions of the form

$$\varphi_1(\alpha;\ \beta) = G^{-1/2} \exp\left\{-\frac{i}{\hbar} d\left(\mathbf{K},\ \frac{\mathbf{g}+\mathbf{f}}{2}\right)\right\} \tag{3.4}$$

$$\times \Phi_{K,\ \rho}(\mathbf{g} - \mathbf{f};\ a,\ b)\,S_{\sigma\tau}(s,\ t),\ \lambda_1 = \lambda_{\mathbf{exc}}(\mathbf{K},\ \rho,\ \sigma,\ \tau),$$

where $\mathbf{K}$ is the quasi-momentum of the exciton, d the lattice constant, ρ the set of discrete quantum numbers, G the number of elementary cells in the fundamental volume of the crystal, and Φ a function which drops rapidly with increasing $|\mathbf{g}-\mathbf{f}|$.

The solutions (3.4) correspond to free excitons, not localized on a defect. It is known (*cf.* for example, Ref. 12) that local exciton levels in the vicinity of a structural defect can also occur. The latter are obviously described by functions of the form

$$\varphi_1(\alpha;\beta) = S_{\sigma\tau}(s,t)\,\Phi_\rho(\mathbf{g},a;\mathbf{f},b),\ \lambda = \lambda_{\mathrm{exc}}(\rho,\sigma,\tau), \tag{3.5}$$

where Φ drops rapidly with increasing $|\mathbf{g}|$ and $|\mathbf{f}|$. (We are considering a structural defect of atomic type, located at the origin of coordinates.)

It is extremely important that in such a formulation of the problem the states describing both the exciton and the free electron and hole are obtained from solutions of the same equation. It is also important to remark that excited states are taken into account in (2.3), so that we are considering all those effects which, in the phenomenological treatment of the problem, are described by means of the dielectric constant. Thus the excitons which we are discussing here are real excitons, observable in experiment, and not the virtual excitons which in Toyozawa's[7] treatment give rise to the dielectric constant of the crystal.* This is precisely the point of basic difference between the theory presented in the present paper and that of Ref. 7.

4. TRANSITION PROBABILITY

For the calculation of the transition probability it is convenient (though not necessary) to specialize the system somewhat. We shall consider a semiconductor containing structural defects of atomic type (impurity atoms, vacancies, *etc.*). We shall assume that in the ground state the corresponding local levels are filled. The structural defects may be either neutral or charged, depending on the nature of the sample and the particular defect, and also on the content and composition of other impurities. We shall treat the capture of free holes. Then the initial state is described by a wave function ψ_1, where $\varphi_1(\alpha;\beta)$ is a function of the type of (3.1) (describing a free electron and hole). The final state is ψ_2, where φ_2 corresponds to the presence of a free electron, a hole localized on the defect, and an exciton. In accordance with our remarks in Sec. 2, this means that φ_2 has the form (N is a normalization factor):

$$\varphi_2^{\lambda_2}(\alpha_1,\alpha_2;\beta_2,\beta_1) = \frac{1}{4\sqrt{N}}\{\varphi_1^{\lambda_1'}(\alpha_1;\beta_1)\,\varphi_1^{\lambda_1''}(\alpha_2;\beta_2)$$

$$-\varphi_1^{\lambda_1'}(\alpha_1;\beta_2)\,\varphi_1^{\lambda_1''}(\alpha_2;\beta_1) + \varphi_1^{\lambda_1''}(\alpha_1;\beta_1)\,\varphi_1^{\lambda_1'}(\alpha_2;\beta_2) - \varphi_1^{\lambda_1''}(\alpha_1;\beta_2)\,\varphi_1^{\lambda_1'}(\alpha_2;\beta_1)\}, \tag{4.1}$$

$$\lambda_2 = \lambda_1' + \lambda_1'';\quad \lambda_1' = \lambda_n + \lambda_p,\quad \lambda_1'' = \lambda_{\mathrm{exc}}, \tag{4.2}$$

while the functions φ_1 in (4.1) have the form of either (3.1), (3.2) (for λ_1'), or (3.4), (3.5) (for λ_1''). The free electron, which is present in both the initial and final states, is included because, by the very nature of the construction of the function (2.1), excitations occur only subject to conservation of the total charge of the system. This electron, however, does not participate in the process of capture of the hole (as long as we do not consider the process of collisional recombination which, by the way could also be investigated by the method given here). Therefore, only the last two terms in the matrix element (2.5) are important; in addition, in our case we can neglect exchange between electrons (but not between holes). Then, using the antisymmetry of B, we obtain

$$H_{21} = -2N^{-1/2}\sum_{\alpha_1,\,\alpha_2}\ \sum_{\beta_1,\,\beta_2}\overline{\varphi}_1^{\lambda_1'}(\alpha_1;\beta_1)\,\overline{\varphi}_1^{\lambda_1''}(\alpha_2;\beta_2)$$

$$\times\,\varphi_1^{\lambda_1}(\alpha_1;\beta)\,B(\beta,\alpha_2;\beta_2,\beta_1), \tag{4.3}$$

(λ_1 is the energy of the system in the initial state). The matrix element $B(\beta,\alpha_2;\beta_2,\beta_1)$ has the form:[8]

$$B(\beta,\alpha_2;\beta_2,\beta_1) = \delta_{tt_2}\delta_{s_2t_1}G'_{ba_2;\,b_2b_1}(\mathbf{f},\mathbf{g}_2;\ \mathbf{f}_2\mathbf{f}_1)$$

$$-\,\delta_{tt_1}\delta_{s_2t_2}G''_{ba_2;\,b_2b_1}(\mathbf{f},\mathbf{g}_2;\ \mathbf{f}_2,\mathbf{f}_1), \tag{4.4}$$

where G' and G'' are integrals containing the Coulomb potential and quasi-atomic functions.

Substituting (4.4) and the functions φ_1 in (4.3)

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*In crystals of the germanium type, the difference between the two kinds of excitons is by no means small, since the dielectric constant is 16!

and summing over α_1, we find, within the approximation given by (3.3),

$$H_{21} = -N^{-1/2} \sum_{b, b_1, b_2, a_2} \sum_{\mathbf{f}, \mathbf{g}_2} \bar{\chi}_p^{\nu_1}(b_1)\, \bar{\Phi}_{K,\rho}(a_2; b_2)\, \chi_p^{\nu}(b)$$
$$\times \exp\left[\frac{i}{\hbar} d(\mathbf{K}, \mathbf{g}_2)\right] F_p(\mathbf{f}) \{\delta_{\tau_1\sigma_2} \delta_{\tau_2\tau} G'_{ba_2;b_2b_1}(\mathbf{f}, \mathbf{g}_2; \mathbf{g}_2, 0)$$
$$- \delta_{\tau_1\tau}\delta_{\sigma_2\tau_2} G''_{ba_2;\, b_2b_1}(\mathbf{f}, \mathbf{g}_2; \mathbf{g}_2, 0)\} \qquad (4.5)$$

(where $F_p(\mathbf{f})$ is the hole wave function in the continuous spectrum for zero quasi-momentum).

No satisfactory explicit evaluation of the sum (4.5) is possible. However, this is not necessary for our purposes since, by virtue of the approximation (3.3) (*i.e.*, for deep traps), no quantities appear which depend on the quasi-momentum of the captured hole (and which would, when averaged over the equilibrium distribution of holes, lead to a dependence of the transition probability on temperature). What is of interest is the dependence of the transition probability on the quasi-momentum of the emitted exciton (*i.e.*, in the final analysis, on the depth of the trap). This dependence can be determined if $dK/\hbar \ll 1$, *i.e.*, if the depth of the trap is sufficiently close to the minimum energy of excitation of the exciton. Actually, it is easy to verify that G' is always an exchange integral, while G'' is either an exchange or a Coulomb integral, depending on the values of $\mathbf{f}$ and $\mathbf{g}_2$. In the first case, only small values of $\mathbf{g}_2$ are important, and consequently $\exp[id(\mathbf{K}, \mathbf{g}_2)/\hbar] \approx 1$. In the second case the corresponding sum can be approximately replaced by an integral which is easily evaluated, since the main contributions to it come from large distances r for which the Coulomb integral is $\sim 1/r$. Thus we get:

$$H_{21} \cong \delta_{\tau_1\sigma_2}\delta_{\tau_2\tau} a(\nu_1, \nu, \rho) -$$
$$- \delta_{\tau_1\tau}\delta_{\sigma_2\tau_2}\{(\hbar / dK)^2 b(\nu_1, \nu, \rho) + c(\nu_1, \nu, \rho)\}, \qquad (4.6)$$

where a, b, c are constants having the dimensions of an energy.

Formula (4.6) is valid for non-localized excitons. If localized excitons are emitted, then we must use the wave function (3.5) instead of (3.4). The corresponding quantity H_{21} can also be written in the form of (4.6) by setting $b = 0$.

We thus find for the transition probability

$$P(1 \to 2)$$
$$= (2\pi / \hbar)\, \delta(\lambda_{\mathbf{exc}} - J - \lambda_p) \{\delta_{\tau_1\sigma_2}\delta_{\tau_2\tau} | a(\nu_1, \nu, \rho)|^2$$
$$+ \delta_{\tau_1\tau}\delta_{\sigma_2\tau_2} | (\hbar / dK)^2 b(\nu_1, \nu, \rho) + c(\nu_1, \nu, \rho)|^2 \qquad (4.7)$$
$$+ \delta_{\sigma\tau}\delta_{\tau\tau_1}\delta_{\tau\tau_2} [a(\nu_1, \nu, \rho)((\hbar / dK)^2 \bar{b}(\nu_1, \nu, \rho)$$
$$+ \bar{c}(\nu_1, \nu, \rho)) + \text{comp. conj.}]\}.$$

It is easily seen that the last two terms in the curly brackets refer only to emission of excitons with zero spin, while the first term corresponds to emission of excitons with arbitrary spin.

For the further development, it is convenient to make some sort of assumption concerning the shape of the spectrum of the free exciton. The simplest form is

$$\lambda_{\mathrm{exc}} = \lambda_0(\rho) + K^2 / 2M(\rho), \qquad (4.8)$$

where λ_0 and M are constants which in general depend on the spin of the exciton.

We must emphasize that the basis for this approximation is much poorer than that of all the preceding approximations; however we must remember that it affects only the dependence of the effective cross section on the depth of the trap but does not affect the temperature dependence of the recombination coefficient.

If we now sum over the quasi-momentum of the exciton (for the case of emission of non-localized excitons) and also over the spins and other quantum numbers of the quasi-particles in the final state, we get the effective capture cross section for holes, σ_p:

a) with emission of non-localized excitons of spin one (V_0 is the volume of the elementary cell, and v the velocity of the captured hole):

$$\sigma_p = (V_0^2 / \hbar^4 v) \sum_{\rho} M^{3/2} (J + \lambda_p - \lambda_0)^{1/2} A_\nu(\rho); \qquad (4.9)$$

b) with emission of non-localized excitons of spin zero,

$$\sigma_p \cong (V_0^2 / \hbar^4 v) \sum_{\rho} \frac{\hbar^4 B_\nu(\rho)}{d^4 M^{1/2} (J + \lambda_p - \lambda_0)^{3/2}}; \qquad (4.10)$$

c) with emission of localized excitons of arbitrary spin,

$$\sigma_p = (V_0 / \hbar v) \sum_{\rho} C_\nu (\rho)\, \delta\, [\lambda_{\mathrm{exc}}(\rho) - J - \lambda_p]. \tag{4.11}$$

Here A, B, C are constants having dimensions of the square of an energy; the subscript ν indicates the "type" of hole.

5. RECOMBINATION COEFFICIENTS. CONCLUDING REMARKS

The quantities of experimental interest are not the capture cross sections themselves, but rather the recombination coefficients c_n and c_p, which are defined[12] as the average values of $\sigma_n v$ and $\sigma_p v$ over the equilibrium distribution of current carriers in the respective bands. On the basis of (4.9) – (4.11) we get:

a) with emission of non-localized excitons of spin one,

$$c_p = \frac{V_0^2}{2\hbar^4} \Big\{ \sum_{\rho,\, \lambda_0 (\rho) < J} M^{3/2} (J - \lambda_0)^{1/2} A_\nu / \rho) + \sum_{\rho,\, \lambda_0 (\rho) > J} M^{3/2} (\lambda_0 - J)^{1/2} A'_\nu (\rho) \exp\left(-\frac{\lambda_0 - J}{kT}\right)\Big\}; \tag{5.1}$$

b) with emission of non-localized excitons of spin zero,

$$c_p = \frac{V_0^2}{2d^4} \Big\{ \sum_{\rho,\, \lambda_0 (\rho) < J} \frac{B_\nu (\rho)}{M^{1/2} (J - \lambda_0)^{3/2}} + \sum_{\rho,\, \lambda_0 (\rho) > J} \frac{B'_\nu (\rho) (\lambda_0 - J)^{1/2}}{M^{1/2} (kT)^2} \exp\left(-\frac{\lambda_0 - J}{kT}\right)\Big\}; \tag{5.2}$$

c) with emission of localized excitons,

$$c_p = \frac{V_0}{\hbar\, (kT)^{3/2}} \sum_{\rho,\, \lambda_{\mathrm{exc}}(\rho) \geqslant J} C_\nu (\rho) (\lambda_{\mathrm{exc}} - J)^{1/2} \exp\left(-\frac{\lambda_{\mathrm{exc}} - J}{kT}\right). \tag{5.3}$$

These same formulas (with different constants, of course) also hold for c_n.

We emphasize that actually only the first terms in the series (5.1) – (5.3) are important, since for the small radius excitons which we are considering the levels for internal motion are relatively widely separated from one another. We may therefore assume approximately that, for example for the emission of non-localized excitons,

$$c_p = \text{const}, \quad \text{if} \quad \lambda_0 < J, \qquad c_p \sim \exp\left(-\frac{\lambda_0 - J}{kT}\right), \quad \text{if} \quad \lambda_0 > J, \tag{5.4}$$

where const denotes a quantity independent of temperature, while λ_0 is the minimum energy of a "real" exciton.

The apparent discrepancy for $J = \lambda_0$ has, of course, no real significance: actually for $J = \lambda_0$ small quantities of the type which we neglected before are left in the denominator. However, the theory actually does give a resonant increase in the capture cross section and the recombination coefficients when $J \approx \lambda_0$. This conclusion could be checked experimentally, if we could succeed in observing the exciton absorption of light in crystals of the type considered here (or if we studied processes of capture of excitons in molecular crystals). We should emphasize that from the mere existence of exciton states it does not necessarily follow that there is exciton absorption of light; also the probability of this process may turn out to be small.

The order of magnitude of the constants which appear in (5.1) – (5.3) depends essentially on the specific model for the capturing center, so that it is exceedingly difficult to evaluate. Nevertheless it can be shown that if there is no Coulomb repulsion between the current carrier and the structure defect, then even with the strictest assumptions the capture cross section turns out to be not less than 10^{-16} cm^2 (and actually this estimate is on the low side, possibly even by a large factor).

Of particular interest for comparison with experiment is the temperature dependence of the recombination coefficients. As we see from (5.1) – (5.3), for capture with emission of non-localized excitons, c_n and c_p are independent of temperature (to terms of order a^2/L^2 and kT/J), as soon as $\lambda_0 < J$. On the other hand, for $\lambda_0 > J$ and also for emission of localized excitons there is an exponential rise of the recombination coefficients upon heating. A dependence of this type has actually been observed in germanium alloyed with copper[14] and with nickel;[15] in the first case the observations are on capture of electrons, in the second they are for both electrons and holes. The latter case is especially interesting, since considerations associated with the presence of a Coulomb barrier can hardly apply here: the holes are captured by negatively charged traps.

We note that if capture with emission of localized excitons actually plays an important role, then the corresponding traps should serve not only as recombination centers but also as attachment levels (with a short time constant). In fact, as soon as the energy liberated during capture of the current carrier remains localized near the capturing center, there is a considerable probability for the inverse transition to occur with ejection of the localized carrier into the corresponding band. (This remark applies not only to the exciton mechanism for capture, but in general to all cases where the liberated energy is at least temporarily localized near the trap. This may, for example, also be the case for capture with transfer of the energy to local lattice oscillations which are generated in the neighborhood of the defect.[15])

If the local exciton levels lie below all the others, then the ratio of the probabilities for the various effects of the trap should depend markedly on temperature. In fact, if the exciton manages to go over from the localized to the free state (for example, by virtue of its interaction with the lattice), then the trap functions essentially as a recombination center; in the contrary case (where the average time for transition of the exciton into a non-localized form is large compared to the lifetime of the carrier in the trap), the trap plays the part of an attachment level.* Since under our conditions the probability of a transition of the exciton into the continuous spectrum is proportional to $\exp\{-\Delta\lambda/kT\}$, where $\Delta\lambda\ (>0)$ is the distance between the bottom of the exciton band and the local exciton level, it is clear that heating should result in stronger "recombinational" action of the capturing center. Careful treatment of the interaction of the exciton with the lattice is essential for a more detailed investigation of this question. However, we emphasize that our whole discussion applies only to attachment levels with a short time constant. The nature of the levels on which current carriers "sit" for a few seconds or even more[16,17] cannot of course be explained in this way.

We remark in conclusion that, as is now completely clear, radiationless electron transitions can be the result of a variety of different causes: the energy can be transferred directly to the lattice, to another current carrier, to plasma oscillations, or finally to excitons. The second and third of the processes listed are relatively easy to distinguish, since the corresponding recombination coefficients depend specifically on the concentration of current carriers. As for the first and fourth possibilities, they apparently can be distinguished only by the temperature dependence of their recombination coefficients. It therefore seems to us that the investigation of the concentration and temperature dependence of recombination coefficients is one of the most urgent problems for experiment.

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* From this it also follows that there is, in general, no sharp dividing line between attachment levels and recombination centers; there can be a continuous transition from one type to the other.

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