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Translated by H. Lashinsky
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SOVIET PHYSICS JETP VOLUME 4, NUMBER 4 MAY, 1957

On the Theory of Atomic Semiconductors

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(Submitted to JETP editor July 6, 1955)
J. Exptl. Theoret. Phys. (U.S.S.R.) 31, 596-608 (October, 1956)

On the basis of Vonsovskii's polar model of crystals several questions in the theory of absorption of light and the theory of photoconductivity in atomic semiconductors are examined, taking excitons into account. We consider terms of third order in the Hamiltonian, which determine the probability of different transitions among the elementary forms of excitation; this allows an examination of the kinetics of photoconductivity.

1. INTRODUCTION

THE polar model of crystals was proposed in 1934 by Shubin and Vonsovskii[1]. In this model the semiconductor in the normal state is considered as an ideal monocrystal, at the lattice sites of which are atoms with one valence *s*-electron. In the excited state sites can occur at which there are two electrons, and correspondingly, empty sites. The appearance of this type of excited state causes its electrical conductivity. Actually, on account of the translational symmetry, the states of the sites in which there are two electrons (or, respectively, none) can propagate through the crystal, which leads to the appearance of degenerate states. Since each state with definite sites occupied by two electrons, or with empty sites, is quasi-stationary, we obtain a whole band of energy levels. In this way the energy spectrum of an atomic semiconductor, from the point of view of the polar model, can even be continuous; but since the excitation of states with double and empty sites requires an expenditure of energy, the excitation of current states in the crystal requires a known activation energy, in spite of the existence of the continous spectrum. Thus, for example, if one considers the exchange interaction between the electrons, the energy spectrum of the crystal has the form shown in Fig. 1, from which it can be seen that the conduction states occurring in the upper band, overlapping the lower one (due to the exchange interaction), require an activation energy for their excitation.

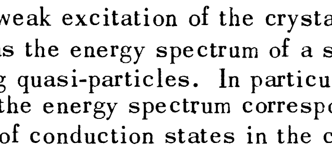

FIG. 1. *1* – Nonconduction band; *2* – Conduction band.

It is known[2] that an energy spectrum of this form (for weak excitation of the crystal) can be regarded as the energy spectrum of a system of non-interacting quasi-particles. In particular, the branch of the energy spectrum corresponding to the existence of conduction states in the crystal can be considered as the energy spectrum of a collection of positively charged (holes) and negatively charged (doublets) quasi-particles.

Besides the types of excitation of the crystal mentioned above there are states possible in which the electron in one or several atoms is found in an excited state. To such states, on account of translational degeneracy, there also corresponds a definite energy band. The corresponding quasi-particles are called Frenkel excitons. It is not difficult to show by a simple calculation (this, by the way, is also obvious physically) that the Frenkel excitons form currentless states (i.e., these quasi-particles are electrically neutral).

In what follows we shall neglect the exchange energy. This leads to the result that the lower energy band of the spectrum represented in Fig. 1 and corresponding to the currentless states degenerates into a single energy level, separated by a gap from the band of excited states. Assuming that the excitation energy of the excitons is greater than the excitation energy of the conduction states, we obtain an overlapping (in the upper part) of the exciton energy band and the energy band corresponding to the conduction states (Fig. 2).

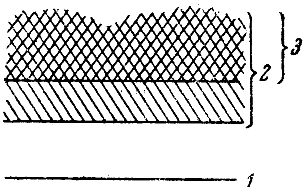

FIG. 2. *1* – Nonconducting state; *2* – Conduction band; *3* – Exciton band.

2. THE HAMILTONIAN OF AN ATOMIC SEMICONDUCTOR ON THE POLAR MODEL

We shall introduce the basic features of the derivation of the Hamiltonian for the polar model of semiconductors and analyze the physical meaning of the results obtained.

We shall proceed from the well-known representation of the Hamiltonian in terms of quantized wave functions:

$$H = \int \Psi^+(x) H(x) \Psi(x)\,dx + {}^1/_2 \int \Psi^+(x)\Psi^+(x') G(|\mathbf{r}-\mathbf{r}'|)\Psi(x')\Psi(x)\,dx\,dx', \quad (2.1)$$

$$H(x) = -\frac{\hbar^2}{2m}\nabla^2 + \sum_q G(|\mathbf{r}-\mathbf{R}_q|) \quad (2.2)$$

is the Hamiltonian of an electron moving in the force field of all the ions; $G(|\mathbf{r}-\mathbf{R}_q|)$ is the potential of an ion located at site q;

$$G(|\mathbf{r}-\mathbf{r}'|) = e^2/|\mathbf{r}-\mathbf{r}'| \quad (2.3)$$

is the potential energy of interaction of two electrons. The quantized wave functions have the form

$$\Psi(x) = \sum_k a_k \psi_k(x); \quad \Psi^+(x) = \sum_k a_k^+ \psi_k^*(x), \quad (2.4)$$

where a_k^+, a_k are the usual operators of the second quantization for the electrons (Fermi amplitudes), $\psi_k(x)$ is a complete orthogonalized system of functions; the summation is taken over all possible states of the electron. Substituting (2.4) into (2.1) we obtain the well-known expression for the Hamiltonian of a system of electrons in terms of Fermi operators

$$H = \sum_{kl} (k \mid H \mid l)\, a_k^+ a_l + \frac{1}{2}\sum_{klps} (kl \mid G \mid ps)\, a_k^+ a_l^+ a_s a_p. \quad (2.5)$$

The matrix elements are determined by the expressions

$$(k \mid H \mid l) = \int \psi_k^*(x) H(x) \psi_l(x)\,dx, \quad (2.6)$$

$$(kl \mid G \mid ps) = \int \psi_k^*(x)\psi_l^*(x') G(|\mathbf{r}-\mathbf{r}'|)\psi_p(x)\psi_s(x')\,dx\,dx'. \quad (2.7)$$

In the polar model of atomic semiconductors one proceeds from the following approximation. The operator (2.5) is taken as being the Hamiltonian, but in calculating the matrix elements, the atomic wave functions, i.e., the wave functions of the isolated atoms, are used. Here, if it is necessary to consider the existence of exciton states, not only the wave functions of the normal state but also the wave functions of the first excited state are taken into account. This system of functions is not complete.

Furthermore, functions referring to different atoms are nonorthogonal. In this way, strictly speaking, the expression for the Hamiltonian (2.5), computed by use of atomic functions, is inexact. However, considering that the wave functions of different atoms overlap weakly, their nonorthogonality is neglected in the polar theory of semiconductors. It would be more nearly correct to orthogonalize the system of atomic wave functions by the method of Bogoliubov[3]; however, this will not be done in this work. We should have a complete system of functions if we considered all possible excited states of the atoms. The incompleteness of the system of functions used apparently does not have any essential significance in the majority of cases.

Thus we put

$$\psi_k(x) = \varphi_i(\mathbf{r} - \mathbf{R}_q)\, u_t(\sigma), \tag{2.8}$$

where $i = 0$ corresponds to the ground state, $i = 1$ to the excited state of the atom, $u_t(\sigma)$ is the spin function [in Eqs. (2.1)-(2.7) we understand by x the collection of space and spin-coordinates]. Calculating the matrix elements by means of such functions and substituting them into (2.5) we obtain, after summing over spins,

$$H = \sum H_{q_1 i_1;\, q_2 i_2} a^{+}_{q_1 i_1 s} a_{q_2 i_2 s} \tag{2.9}$$

$$+ \frac{1}{2} \sum I_{q_1 i_1;\, q_2 i_2;\, q_3 i_3;\, q_4 i_4}\, a^{+}_{q_1 i_1 s} a^{+}_{q_2 i_2 s'} a_{q_4 i_4 s'} a_{q_3 i_3 s}, \tag{2.10}$$

$$H_{q_1 i_1;\, q_2 i_2} = \int \varphi^{*}_{i_1}(\mathbf{r} - \mathbf{R}_1)\, H(r)\, \varphi_{i_2}(\mathbf{r} - \mathbf{R}_{q_2})\, d\tau$$

[$H(r)$ in fact coincides with $H(x)$, since the spin variables do not enter into the last expression].

$$I_{q_1 i_1;\, q_2 i_2;\, q_3 i_3;\, q_4 i_4} \tag{2.11}$$

$$= \int \varphi^{*}_{i_1}(\mathbf{r} - \mathbf{R}_{q_1})\, \varphi^{*}_{i_2}(\mathbf{r}' - \mathbf{R}_{q_2})$$

$$\times G(|\mathbf{r} - \mathbf{r}'|)\, \varphi_{i_3}(\mathbf{r} - \mathbf{R}_{q_3})\, \varphi_{i_4}(\mathbf{r}' - \mathbf{R}_{q_4})\, d\tau\, d\tau'.$$

As is well known, the Fermi operators a^{+}_{qis} and a_{qis} act on wave functions, the arguments of which are the occupation numbers of the electronic states $C(n_{qis})$. In the polar model the states of the crystal are characterized by the states of the lattice sites. Let us introduce the symbols

$$R_q = \begin{cases} 1 & \text{when one electron with a right-hand spin is at site } q, \\ 0 & \text{in all remaining cases} \end{cases}$$

and analogously, L_q for an electron with a left-hand spin, E^{+}_q for an empty site, E^{-}_q for a site with two electrons, E^{L}_q and E^{R}_q for an excited electron with left- and right-hand spins, respectively.

Clearly, the equation

$$R_q + L_q + E^{+}_q + E^{-}_q + E^{R}_q + E^{L}_q = 1 \tag{2.12}$$

must be satisfied. The quantities R_q, L_q, E^{+}_q can be taken as the dynamical variables of our system, having the meaning of the corresponding occupation numbers. The wave functions then must be considered as functions of these variables.

Let us introduce the operators of the second quantization corresponding to these variables: φ_q, χ_q, Ψ_q, Φ_q, ζ_q, ϑ_q (and those associated with them) act respectively on the variables R_q, L_q, E^{+}_q, E^{-}_q, E^{R}_q, E^{L}_q. Following Shubin and Vonsovskii[1] we assume that these operators obey the Bose commutation relations.

For the transformation of the Hamiltonian (2.9) to these operators, we proceed in the following way. We designate by $C_0 = C(1, 0; 1, 0; 1, 0; \ldots)$ the wave function of the "zero-order" state (one electron with a left-hand spin on each atom). Then a function of the form

$$C = \prod_{i=1}^{s} C^{+}_{g_i} a^{+}_{f_i} \prod_{l=1}^{u} C^{+}_{h_l} a^{+}_{h_l} \varepsilon(\ldots;\, 1,0;\, \ldots)\, C_0 \tag{2.13}$$

$$= \varepsilon(f_1 \ldots f_s;\, g_1 \ldots g_s;\, r_1 \ldots r_m;\, h_1 \ldots h_n)$$

$$\times \prod_{i=1}^{s} C_{g_i} a^{+}_{f_i} \prod_{l=1}^{u} C^{+} l_{h_l} a^{+}_{h_l} C_0$$

corresponds to the state of the crystal in which at sites $f_1, \ldots f_s$ there are two electrons each (with opposite spins), the sites $g_1, \ldots g_s$ are empty, at the sites $k_1, \ldots h_n$ there is one electron with a right-hand spin, and at the remaining sites $r_1, \ldots r_m$ there is one electron with a left-hand spin. Here $C_{gi} = a^{+}_{gi, -1/2}$; $a^{+}_{fi} = a^{+}_{fi, 1/2}$. The function

$$\varepsilon(f_1 \ldots f_s;\, g_1 \ldots g_s;\, r_1 \ldots r_m;\, h_1 \ldots h_n) \tag{2.14}$$

$$= \varepsilon(\ldots;\, n^{L}_q, n^{R}_q;\, \ldots)$$

is symmetric in the indices r or h separately and antisymmetric in the indices f or g.

Noting that $C(\ldots n_q, m_q; \ldots) = D(\ldots, R_q, L_q, E^+_q, E^-_q, E^R_q, E^L_q, \ldots)$, it is possible to relate uniquely the result of the action of the Bose operators on the function D to the result of the action of the Fermi operator on the function C. Thus, for example, it is easy to convince oneself that to the operator $a^+_q C_q C_{q'} a_{q'}$ corresponds the operator $\psi_q \Phi^+_q \Phi_{q'} \psi^+_{q'}$.

Omitting all these transformations, we write down immediately the expression for the Hamiltonian in Bose operators without taking into account the excited states of the atom, which is considerably simpler than the complete Hamiltonian, and we show by this example which simplifications are to be used in the sequel. It must also be mentioned that the expression presented below for the Hamiltonian already contains a series of simplifications, inasmuch as terms were discarded which correspond to the simultaneous transition of two or more electrons (the integrals corresponding to such transitions are considerably smaller than the remaining terms). Therefore, for the Hamiltonian in the polar model (without taking into account exciton states) we obtain the well-known Hamiltonian of Vonsovskii[1]

$$\begin{aligned} H = {}& {}^1\!/_2 (A+D) \sum (\Psi^+_q \Psi_q + \Phi^+_q \Phi_q) \qquad (2.15) \\ & + {}^1\!/_2 \sum B_{qq'} (\Psi^+_q \Psi_q - \Phi^+_q \Phi_q)(\Psi^+_{q'} \Psi_{q'} - \Phi^+_{q'} \Phi_{q'}) \\ & + {}^1\!/_2 \sum I_{qq'} (\Phi^+_q \Psi^+_{q'} - \Psi^+_q \Phi^+_{q'}) (\Phi_q \Psi_{q'} - \Psi_q \Phi_{q'}) \\ & - {}^1\!/_2 \sum I_{qq'} (\Psi^+_q \Psi_q + \Phi^+_q \Phi_q) (\Psi^+_{q'} \Psi_{q'} + \Phi^+_{q'} \Phi_{q'}) \\ & + {}^1\!/_2 \sum I_{qq'} (\chi^+_{q'} \varphi^+_q - \chi^+_q \varphi^+_{q'})(\chi^+_{q'} \varphi_q - \chi_q \varphi_{q'}) \\ & + {}^1\!/_2 \sum L_{qq'} [(\varphi_q \varphi^+_{q'} + \chi_q \chi^+_{q'})(\Phi^+_q \Phi_{q'} - \psi^+_q \Psi_{q'}) \\ & \qquad + (\varphi_{q'} \varphi^+_q + \chi_{q'} \chi^+_q) (\Phi^+_{q'} \Phi_q - \Psi^+_{q'} \Psi_q)] \\ & + {}^1\!/_2 \sum L_{qq'} [(\varphi_q \chi_{q'} - \chi_q \varphi_{q'}) (\Phi^+_q \Psi^+_{q'} \\ & - \Phi^+_{q'} \Psi^+_q) + (\varphi^+_q \chi^+_{q'} - \chi^+_q \varphi^+_{q'}) (\Phi_q \Psi_{q'} - \Psi_q \Phi_{q'})] \end{aligned}$$

(the summations are over all indices q, q').

In what follows we shall examine cases in which the number of excitations is small; in other words, in which at the majority of lattice sites simple atoms with right- and left-hand spins occur, whereby both directions of spin are considered equally probable. Therefore, $\overline{\varphi^+_q \varphi_q} \sim 1/2$ and $\overline{\chi^+_q \chi_q} \sim 1/2$, where the bar designates the average value. Since the number of simple atoms is considerably larger than the number of empty and double sites, we can neglect the changes of state of the collection of simple atoms in the occurrence of these and other excitations; and we can consider this collection of simple atoms as a classical system, a special reservoir, from which can arise empty and double sites, but the states of which do not change thereby. This is somewhat analogous, on the one hand, to the introduction of a thermostat in the derivation of the Gibbs distribution; or, on the other hand, it is analogous to the classical representation of radiation of great intensity in the quantum representation of the absorbing atom. In the latter case the radiation is considered classically and is described by commuting quantities. Analogously, in our case, considering the collection of simple atoms as a classical system, we can consider operators referring to the simple atoms as commuting quantities, and in correspondence with this we put

$$\varphi^+_q = \varphi_q = \chi^+_q = \chi_q = 2^{-1/2}. \qquad (2.16)$$

Hence, the Hamiltonian (2.15) simplifies and takes the following form:

$$\begin{aligned} H = {}& {}^1\!/_2 (A+D) \sum (\Psi^+_q \Psi_q + \Phi^+_q \Phi_q) \qquad (2.17) \\ & + {}^1\!/_2 \sum B_{qq'} (\Psi^+_q \Psi_q - \Phi^+_q \Phi_q) (\Psi^+_{q'} \Psi_{q'} - \Phi^+_q \Phi_{q'}) \\ & + {}^1\!/_2 \sum I_{qq'} (\Phi^+_q \Psi^+_{q'} - \Psi^+_q \Phi^+_{q'}) (\Phi_q \Psi_{q'} - \Psi_q \Phi_{q'}) \\ & - {}^1\!/_2 \sum I_{qq'} (\Psi^+_q \Psi_q + \Phi^+_q \Phi_q) (\Psi^+_{q'} \Psi_{q'} + \Phi^+_{q'} \Phi_{q'}) \\ & + {}^1\!/_2 \sum L_{qq'} [\Phi^+_q \Phi_{q'} + \Phi^+_{q'} \Phi_q - \Psi^+_q \Psi_{q'} - \Psi^+_{q'} \Psi_q]. \end{aligned}$$

In this approximation the principal feature is the circumstance that the operators of creation and annihilation of empty and double sites disappear, so that in this approximation the average number of the latter is an integral of the motion. Further, an additional approximation occurs, which results in the fact that in the operator (2.17) only terms quadratic in the operators remain, i.e., the energy of mutual interaction of the excitations is neglected, considering the number of excitations small. Then in place of (2.17), we obtain

$$H = {}^1/_2 (A + D) \sum (\psi_q^+ \psi_q + \Phi_q^+ \Phi_q) \tag{2.18}$$
$$+ {}^1/_2 \sum L_{qq'} (\Phi_q^+ \Phi_{q'} + \Phi_q^+ \Phi_q - \Psi_q^+ \Psi_{q'} - \Psi_{q'}^+ \Psi_q).$$

The expression for the Hamiltonian, considering the exciton states of the atoms and corresponding to (2.15), is too cumbersome, and we shall not present it here. Below is given the expression for the Hamiltonian, taking into account the exciton states, in the approximation corresponding to (2.18), with, however, this difference: that in it are included terms of the third order relative to the operators of second quantization:

$$H = H_{(2)} + H_{(3)}, \tag{2.19}$$

$$H_{(2)} = Q^{(1)} \sum (\alpha_q^+ \alpha_q + \beta_q^+ \beta_q) \tag{2.20}$$
$$+ Q^{(2)} \sum (\Psi_q^+ \Psi_q + \Phi_q^+ \Phi_q)$$
$$+ \sum Q_{fq}^{(3)} (\alpha_q^+ \alpha_f + \alpha_q \alpha_f^+) + \sum Q_{fq}^{(3)} (\beta_q^+ \beta_f + \beta_q \beta_f^+)$$
$$+ \sum Q_{fq}^{(4)} (\Phi_q^+ \Phi_f + \Phi_f^+ \Phi_q)$$
$$- \sum Q_{fq}^{(4)} (\Psi_q^+ \Psi_f + \Psi_q \Psi_f^+);$$

$$H_{(3)} = \sum N_{fq}^{(1)} [\psi_q^+ \psi_f (\alpha_q - \beta_q) + \psi_q \psi_f^+ (\alpha_q^+ - \beta_q^+)] \tag{2.21}$$
$$+ \sum N_{fq}^{(2)} [\Phi_q^+ \Phi_f (\alpha_q - \beta_q) + \Phi_q \Phi_f^+ (\alpha_q - \beta_q)]$$
$$+ \sum N_{fq}^{(3)} [\Psi_q^+ \Phi_f^+ (\alpha_q + \beta_q) + \Psi_q \Phi_f (\alpha_q^+ + \beta_q^+)]$$
$$+ \sum N_{fq}^{(4)} [\Phi_q^+ \Psi_f^+ (\alpha_q + \beta_q) + \Phi_q \Psi_f (\alpha_q^+ + \beta_q^+)]$$
$$+ \sum N_{fq}^{(5)} (\beta_q^+ \beta_q + \alpha_q^+ \alpha_q) (\alpha_f + \alpha_f^+ - \beta_f - \beta_f^+)$$
$$+ \sum N_{fq}^{(6)} (\Psi_f^+ \Psi_f - \Phi_f^+ \Phi_f) (\alpha_q + \alpha_q^+ - \beta_q - \beta_q^+)],$$

Q and N are certain coefficients, the form of which we shall not write down in the present article.

The operators α_q, α_q^+, β_q^+, β_q^+ are the operators for the left-hand and right-hand excited sites (exciton sites) which are connected with the operators of the excited sites presented earlier by the relations

$$\vartheta_q = \alpha_q + c, \quad \vartheta_q^+ = \alpha_q^+ + c, \tag{2.22}$$

$$\zeta_q = \beta_q - c, \quad \zeta_q^+ = \beta_q^+ - c,$$

where c is a certain constant, chosen in a definite way. It is necessary to carry out the transformation (2.22) in order that terms in the Hamiltonian of first order relative to the operators disappear.

The physical meaning of the quadratic and third order terms in the operators is more easily explained after the transformation of the Hamiltonian to the space of quasi-momenta and the introduction of the corresponding quasi-particles.

3. TRANSFORMATION TO THE SPACE OF QUASI-MOMENTA

For the transition to the space of quasi-momenta we introduce the following canonical transformation:

$$\Psi_q = N^{-1/2} \sum_k \Psi_k e^{-i(\mathbf{k} - \pi \mathbf{b}) \mathbf{R}_q}; \tag{3.1}$$

$$\Phi_q = N^{-1/2} \sum_k \Phi_k e^{-i \mathbf{k} \mathbf{R}_q},$$

$$\alpha_q = N^{-1/2} \sum_k \vartheta_k e^{-i \mathbf{k} \mathbf{R}_q},$$

$$\beta_q = N^{-1/2} \sum_k \zeta_k e^{-i \mathbf{k} \mathbf{R}_q},$$

where **b** is a vector of the reciprocal lattice (and analogously for those associated with it). Operators with the indices k, describing processes of creation or annihilation of the corresponding quasi-particles, satisfy the same commutation rules as the operators with indices q. In the Fourier transformation (3.1), the writing of $(\mathbf{k} - \pi \mathbf{b})$ in place of $\mathbf{k}$ for the operator Ψ denotes that the subtraction of the quasi-momenta of the holes is carried out from the upper edge of the band, and not from the lower one, as is done for the doublets and excitons. Thanks to this, we obtain a positive effective mass for the holes.

After carrying out the transformation, we obtain

$$H_{(2)} = \sum_k E'_k n_k^{\vartheta} + \sum_k E'_k n_k^{\zeta} + \sum_k E_k n_k + \sum_k E_k n_k^{\Psi}, \tag{3.2}$$

where $n_k^{\vartheta} = \vartheta_k^+ \vartheta_k$, n_k^{ξ}, n_k^{Ψ} are operators for the occupation numbers of the left-hand excitons, right-hand excitons, doublets and holes. In this way the Hamiltonian (3.2) is presented in the form of the sum of the energies of the elementary excitations.

E'_k, E_k have the meaning of the energies of the corresponding elementary excitations. In the effective-mass approximation they have the form

$$E_k = \Delta E + \hbar^2 k^2 / 2\mu, \quad E'_k = \Delta E' + \hbar^2 k^2 / 2\mu', \tag{3.3}$$

where ΔE is the excitation energy of a doublet or hole, $\Delta E'$ is the energy of excitation of an exciton, μ is the effective mass of a doublet (hole), μ' is the effective mass of an exciton.

As far as the terms of third order are concerned, after transformation to the space of quasi-momenta we obtain

$$\begin{aligned} H_{(3)} = {} & \Sigma K^{(1)}(\mathbf{k}, \mathbf{k}'')\,\delta(\mathbf{k}' - \mathbf{k} - \mathbf{k}'') \\ & \times [\Psi^+_{k'}\Psi_{k''}(\vartheta_k - \zeta_k) + \Psi_{k'}\Psi^+_{k''}(\vartheta^+_k - \zeta^+_k)] \\ & + \Sigma K^{(2)}(\mathbf{k}, \mathbf{k}'')\,\delta(\mathbf{k}' - \mathbf{k} - \mathbf{k}'') \\ & \times [\Phi^+_{k'}\Phi_{k''}(\vartheta_k - \zeta_k) + \Phi_{k'}\Phi^+_{k''}(\vartheta^+_k - \zeta^+_k)] \\ & + \Sigma K^{(3)}(\mathbf{k}', \mathbf{k}'')\,\delta(\mathbf{k}' + \mathbf{k}'' - \pi\mathbf{b} - \mathbf{k}) \\ & \times [\Phi^+_{k'}\Psi^+_{k''}(\vartheta_k + \zeta_k) + \Phi_{k'}\Psi_{k''}(\vartheta^+_k + \zeta^+_k)] \\ & + \Sigma K^{(4)}(\mathbf{k})\,\delta(\mathbf{k}' - \mathbf{k}'' - \mathbf{k}) \\ & \times [(\zeta^+_{k'}\zeta_{k''} + \vartheta^+_{k'}\vartheta_{k''})(\vartheta_k - \zeta_k) \\ & + (\zeta_{k'}\zeta^+_{k''} + \vartheta_{k'}\vartheta^+_{k''})(\vartheta^+_k - \vartheta^+_{k'})] \end{aligned} \tag{3.4}$$

(summation over all indices). The form of the coefficients $K^{(i)}$ is not given here on account of its complexity.

4. ANALYSIS OF SEPARATE TERMS OF THIRD ORDER

The physical meaning of the separate terms of the expression (3.4) can be easily explained directly from the form of the operators. Thus, for example, the term $\Psi^+_{k'}\Psi_{k''}\vartheta_k$ corresponds to the annihilation of a left-hand exciton with quasi-momentum **k**. The energy of the exciton is thereby transferred to a hole with quasi-momentum **k**″, as a result of which the hole acquires a quasi-momentum **k**′. It must be mentioned that this process proceeds with conservation of momentum. The term associated with this one, $\Psi_{k'}\Psi^+_{k''}\vartheta^+_k$, corresponds to the inverse process, the process whereby a left-hand exciton with quasi-momentum **k** arises at the expense of the kinetic energy of a hole with quasi-momentum **k**′. The hole as a result of this process acquires a quasi-momentum **k**″. This process also takes place with conservation of momentum, as, by the way, do all the remaining processes described by the Hamiltonian (3.4).

Great interest attaches to the terms of the Hamiltonian (3.4) containing the operators $\Phi^+_{k'}\Psi^+_{k''}\xi_k$ and $\Phi^+_{k'}\Psi^+_{k''}\vartheta_k$. These operators describe the process of spontaneous annihilation of a right- or left-hand exciton with the quasi-momentum **k**, with simultaneous formation of a doublet with quasi-momentum **k**′ and a hole with quasi-momentum **k**″. The associated operators $\Phi_{k'}\Psi_{k''}\xi^+_k$ and $\Phi_{k'}\Psi_{k''}\vartheta^+_k$ correspond to the inverse processes---processes of production of right-hand and left-hand excitons by recombination of a hole and a doublet. The physical meaning of the remaining operators is also clear from their individual forms.

The Hamiltonian $H_{(3)}$ can be regarded as the perturbation of a system, the stationary state of which is determined by the Hamiltonian $H_{(2)}$. In this way $H_{(3)}$ determines the transitions between the stationary states. The quantities $K^{(i)}(\mathbf{k}, \mathbf{k}', \mathbf{k}'')$ determine the probabilities of the corresponding transitions. The computation of these probabilities will not be given in the present article; however, it is already clear from the Hamiltonian itself how, within the frame of the polar model of atomic semiconductors, one can proceed to the examination of very detailed processes.

5. SOME REMARKS ON THE HAMILTONIAN OF AN EXTERNAL PERTURBATION

Let $U(r, t)$ represent the operator of an external perturbation. We shall write down the Hamiltonian of an external perturbation in terms of the quantized wave functions

$$H' = \int \Psi^+(x)\, U(\mathbf{r}, t)\, \Psi(x)\, dx.$$

Substituting the quantized wave functions into this and summing over spins we get

$$H' = \Sigma U_{q_1 i_1; q_2 i_2}\, a^+_{q_1 i_1 s}\, a_{q_2 i_2 s}, \tag{5.1}$$

where $U_{q_1 i_1; q_2 i_2}$ is the matrix element of the operator $U(r, t)$ computed by means of the atomic wave functions of the normal and first excited states, where $i = 0$ corresponds to the ground state and $i = 1$ to the excited state. a^+, a are the usual Fermi operators of the second quantization for creation and annihilation of the electron at the corresponding site.

Let us examine some of the possible transitions--in the first place, processes not connected with the generation of excitons. Obviously such processes are described by a Hamiltonian of the form

$$H_0' = \sum_{q_1q_2s} U_{q_10;\,q_20}\,[a^+_{q_1\,0s}a_{q_20s} + a^+_{q_20s}a_{q_10s}]. \tag{5.2}$$

After changing to Bose operators we get in the quasi-classical approximation

$$H_0' = {}^1\!/_2 \sum_{qq'} U_{q0q'0}\,(\Phi^+_q\Phi_{q'} + \Phi^+_{q'}\Phi_q - \Psi^+_q\Psi_{q'} - \Psi^+_{q'}\Psi_q). \tag{5.3}$$

Therefore, as before, terms corresponding to the creation and annihilation of doublets and holes disappear in the quasi–classical approximation. From this we immediately obtain the following important result. If the external perturbation is a light wave, then holes and doublets cannot arise upon absorption of the light, i.e., conduction states cannot appear. Consequently, the absorption of light in atomic semiconductors, from the point of view of the proposed theory, is photoelectrically inactive and bears a purely exciton character. If one gives up the quasi-classical approximation, the creation of holes and doublets will be possible; however, the probability of this process will be very small in comparison with the probability of exciton absorption.

As regards processes described by the Hamiltonian (5.3) in the case when the perturbation is a light wave, this Hamiltonian then, as it is not difficult to convince oneself, describes the Compton scattering of light by free doublets and holes. In what follows we shall not be interested in this process.

In order to study the exciton mechanism for absorption of light, it is necessary to put $q_i = q_2$, $i_2 = 0$, $i_1 = 1$ into (5.1); then we obtain

$$H_{01}' = \sum_{qs}[U_{q1q0}\,a^+_{q1s}a_{q0s} + U_{q0q1}\,a^+_{q0s}\,a_{q1s}]. \tag{5.4}$$

Since the matrix element U_{q1q0} is computed by use of real functions, $U_{q0q1} = U_{q1q0}$. Going over to Bose operators and to the quasi-classical approximation, we get

$$H_{01}' = 2^{-1/2}\sum_q U_{q1q0}\,(\alpha_q^+ + \alpha_q) - 2^{-1/2}\sum_q U_{q1q0}\,(\beta_q^+ + \beta_q). \tag{5.5}$$

In the Hamiltonian (5.1) are contained terms describing even more complicated processes, for example, the simultaneous absorption of light with the excitation of an exciton and scattering by holes, etc. However, all these processes have a considerably smaller probability, and in the sequel we shall not consider them either. Here we only remark that from this theory arises the possibility of processes, whereby a light wave causes the annihilation of excitons already existing in the crystal with formation of holes and doublets, which leads to an additional conductivity of the crystal.

If the external perturbation is a static one, for example, the force field of an impurity atom, the latter can also cause a series of transitions between states with the same initial and final energy, for example, the decay of excitons with formation of holes and electrons, etc. The corresponding Hamiltonian can also be obtained from (5.1).

Going over to the Bose operators (and to the quasi-classical approximation) we obtain, after the corresponding transformations,

$$\begin{aligned} H_{01}'' = {}& 2^{-1/2}\Sigma U_{q1q0}\,(\alpha_q + \alpha_q^+ - \beta_q^+ - \beta_q) \\ & + {}^1\!/_2\,\Sigma\, U_{f0q0}\,(\Phi^+_q\Phi_f + \Phi^+_f\Phi_q - \Psi^+_q\Psi_f - \Psi^+_f\Psi_q) \\ & + 2^{-1/2}\,\Sigma\, U_{f1q0}\,[(\beta_f - \alpha_f)\Psi^+_f\Psi_q + (\beta_f^+ - \alpha_f^+)\Psi_f\Psi_q] \\ & + 2^{-1/2}\,\Sigma\, U_{f1q0}\,[(\beta_f + \alpha_f)\,\Psi^+_f\Phi^+_q + (\beta^+_f + \alpha^+_f)\Psi_f\Phi_q]. \end{aligned} \tag{5.6}$$

After the transition to the space of quasi-momenta, it is easy to explain the meaning of each term of the Hamiltonian (5.6). Thus for example, the first term of the Hamiltonian gives those transitions in which the law of conservation of energy cannot be satisfied (they can be considered as virtual transitions). Therefore, in considering processes of interaction and transformation of quasi-particles into each other this term can be discarded. The second term of the Hamiltonian (5.6) describes the scattering of holes and doublets from the impurity site. The quasi-momentum of the doublet or hole in such a process takes on a different value after scattering.

The third term of (5.6) describes the process of annihilation of a right-hand or left-hand exciton at the impurities with transfer of their energy already existing in the crystal to the hole, and the inverse process of the creation of a right- or left-hand exciton at the expense of the kinetic energy of a hole. The analogous process with doublets is impossible, since in this case a two-electron transition would be necessary, which cannot be produced by a static field. From this it follows that that part of the mobility which is caused by the presence of impurities will be different for holes and doublets in exciton semiconductors.

Finally, the fourth term of the Hamiltonian (5.6) describes the process of decay of a right- or left-hand exciton at an impurity site into a doublet and a hole, and the inverse process of formation of a right- or left-hand exciton at the expense of recombination of a hole and a doublet at the impurity site.

6. DERIVATION OF AN EXPRESSION FOR THE PROBABILITY OF DECAY OF AN EXCITON AT AN IMPURITY WITH FORMATION OF A DOUBLET AND A HOLE

Let us consider the decay of an exciton (for example, a left-hand one) at the site of an impurity. We locate the origin of coordinates at this site. From (5.6) it follows that the energy operator of the perturbation K has the form

$$K=2^{-1/2}\Sigma\, U_{q_1q'0}\,\alpha_q\Psi_q^{+}\Phi_{q'}^{+}\,. \tag{6.1}$$

Let $U(\mathbf{r})$ be the perturbing potential of the impurity; then

$$U_{q1q'0}=\int\varphi_1^*(\mathbf{r}-\mathbf{R}_q)\,U(\mathbf{r})\,\varphi_0(\mathbf{r}-\mathbf{R}_{q'})\,d\tau. \tag{6.2}$$

Substituting (6.2) into (6.1) and going over to momentum space we get

$$\begin{aligned}K = ((2\pi)^3\, N^{-1/2}/\sqrt{2V})\sum_{\alpha\beta\gamma}\vartheta_\alpha\Psi_\beta^{+}\Phi_\gamma^{+} \\ \times U(|\mathbf{k}_\gamma+\mathbf{k}_\beta-\mathbf{k}_\alpha-\pi\mathbf{b}|) \\ \times\varphi_1(\mathbf{k}_\beta-\mathbf{k}_\alpha-\pi\mathbf{b})\,\varphi_0(\mathbf{k}_\gamma),\end{aligned} \tag{6.3}$$

where φ_1 and φ_2 are the atomic functions in momentum space, and U is the Fourier component of the potential, determined by the expression

$$\begin{aligned}U(|\mathbf{k}_\gamma+\mathbf{k}_\beta-\mathbf{k}_\alpha-\pi\mathbf{b}|) \\ = 1/V_0\int U(|\mathbf{r}|)\,e^{i(\mathbf{k}_\gamma+\mathbf{k}_\beta-\mathbf{k}_\alpha-\pi\mathbf{b})\mathbf{r}}\,d\tau,\end{aligned} \tag{6.4}$$

where V_0 is the volume associated with one atom.

The transition probability can be computed according to the familiar formula

$$w=(2\pi/h)\int|K_{\lambda\mu}|^2\,\delta(E_\lambda-E_\mu)\,d\mu, \tag{6.5}$$

where $K_{\lambda\mu}$ is the matrix element of the operator (6.3) for the transition between states $\lambda \to \mu$ (exciton → doublet plus hole), and the integration is carried out over all possible finite states. We note that in the case at hand, the law of conservation of momentum is not satisfied, since the decay of the exciton takes place in the force field of the impurity. The law of conservation of energy is taken into account by the δ-function in Eq. (6.5).

Calculating the values of the matrix elements of the operator $\vartheta_\alpha\Psi_\beta^{+}\Phi_\gamma^{+}$, stipulating that there is one exciton present and paying attention to the fact that the average occupation number of holes and doublets is $\ll 1$, we get from Eq. (6.5)

$$\begin{aligned}w=(\pi/\hbar N)\int|\varphi_1(\mathbf{k}_\beta-\mathbf{k}_\alpha-\pi\mathbf{b})|^2\,|\varphi_0(\mathbf{k}_\gamma)|^2 \\ \times U^2(|\mathbf{k}_\gamma+\mathbf{k}_\beta-\mathbf{k}_\alpha-\pi\mathbf{b}|) \\ \times\delta(E_e-\varepsilon_\beta-\varepsilon_\gamma)\,d\mathbf{k}_\beta d\mathbf{k}_\gamma,\end{aligned} \tag{6.6}$$

where E_e is the exciton energy, ϵ_β and ϵ_γ, respectively, the energy of the hole and the doublet. Changing to spherical coordinates in this expression, and carrying out the integration over angles, we get

$$\begin{aligned}W = \frac{4\pi^3\mu_d}{\hbar^3 N\varkappa}\int_0^\alpha k_\beta\,|\varphi_0(k'_\gamma)|^2 \\ \times\int_{|k_\beta-\varkappa|}^{k_\beta+\varkappa}|\varphi_1(y)|^2\int_{|k'_\gamma-y|}^{k'_\gamma+y} zU^2(z)\,dz\,dy\,dk_\beta,\end{aligned} \tag{6.7}$$

$$k'_\gamma=\sqrt{\alpha^2-k_\beta^2}\,;$$

$$\alpha=\sqrt{(2\mu_d/\hbar^2)(h\nu-A)};\quad \varkappa=|\mathbf{k}_\alpha+\pi b|.$$

In Eq. (6.7) $\varphi_1(y)$ represents only the radial part of the wave functions; an averaging has been carried out over the angular part.

If there are few sites of the impurity in the crystal, then the action of each on the excitons will be the same as though there were no other impurity sites. The probability of decay of an exciton in such a crystal into a doublet and a hole will be equal to $w = N_{\mathrm{imp}}W$, where N_{imp} is the number of impurity sites in the crystal. From (6.7) it follows that $W \approx 1/N$, therefore, $w \approx N_{\mathrm{imp}}/N$. In this way the probability of decay of an exciton in the crystal into a doublet and a hole is directly proportional to the concentration of impurities. From this it follows that the photoconductivity of an atomic semiconductor, caused by an impurity, is directly proportional to the concentration of impurities. If the probability of spontaneous decay of an exciton is small, then we shall have principally impurity photoconductivity.

The effective cross section can be computed by the formula given by Sokolov and Ivanenko[4]:

$$\sigma = wV / v_e, \tag{6.8}$$

where v_e is the velocity of the exciton. Using the law of conservation of momentum, we obtain

$$v_e = \Delta E_e / \mu_e c. \tag{6.9}$$

Consequently,

$$\sigma = \frac{4\pi^3 \mu_d \mu_e c V}{\hbar^3 \varkappa \Delta E_e N} \tag{6.10}$$

$$\times \int_0^{\alpha} k_\beta |\varphi_0(k'_\gamma)|^2 \int_{|k_\beta - \varkappa}^{k_\beta + \varkappa} |\varphi_1(y)|^2 \int_{|k'_\gamma - y|}^{k'_\gamma + y} z U^2(z)\, dz\, dy\, dk_\beta.$$

As an example of the application of Eq. (6.10), we consider the decay of an exciton at an empty site. In this case the perturbing potential can be set equal to the potential of an isolated atom (with the opposite sign). Therefore, we put

$$U(r) = \frac{ze^2}{r} - e^2 \int \frac{\rho(\mathbf{r}'')\, dv''}{|\mathbf{r}'' - \mathbf{r}|}, \tag{6.11}$$

where $\rho(\mathbf{r})$ is the density of the distribution of electrons. Let us take

$$\rho(\mathbf{r}) = (z\gamma^3 / 8\pi) e^{-\gamma r}. \tag{6.12}$$

For the rest of the calculation it is necessary to choose definite wave functions. For the evaluation we choose for φ_0 the wave function of a hydrogen atom in the 2*s* state, and for φ_1 that of the 3*p* state[5]. The wave function φ_1 was averaged over angles in the following way. Since *p*-states are triply degenerate, φ_1^2 can be set equal to

$$|\varphi_1|^2 = {}^1/_3 \left(|\varphi_1^{(1)}|^2 + |\varphi_1^{(2)}|^2 + |\varphi_1^{(3)}|^2\right), \tag{6.13}$$

where φ_1^1, φ_1^2, φ_1^3 are the three actual functions for the *p*-state.

Substituting the wave functions and (6.11) into (6.10) we obtain

$$\sigma = \frac{2^{20} 3^5 \pi^2 c \mu_d \mu_e e^4 z^2 n}{\hbar^3 \Delta E_e \lambda_s^3 \lambda_p^5} \, \frac{\alpha^4 (\alpha^2 + \varkappa^2)}{(\alpha^2 + \gamma^2 + \varkappa^2)^2} \cdot \tag{6.14}$$

Determination of the numerical value shows that σ changes within unusually wide limits in its dependence on the choice of the effective charges for the *s*- and *p*-states. The results of such an evaluation, as the parameters λ_p and λ_s are changed, are as follows:

λ_s	10^9	10^9	5×10^8	5×10^8
λ_p	3×10^9	2×10^9	2×10^9	3×10^9
σ(cm^2)	4×10^{-16}	3×10^{-15}	2.5×10^{-14}	3×10^{-15}

This shows that σ is very sensitive to the behavior of the wave functions and that for an actual calculation of σ it is necessary to know the exact atomic wave functions in momentum space.

The existing methods for computing atomic functions (the Hartley-Fock method, the variational method) allow one to compute the atomic functions in configuration space. The analogous problem in momentum space is still not solved; therefore, we cannot exhibit numerical values for σ for concrete cases. However, the result obtained shows that the exciton can decay at an impurity with formation of charge carriers even in the case when the site is empty, i.e., does not contain bound charges in it.

7. KINETICS OF PHOTOCONDUCTIVITY

As was explained in Secs. 5 and 6, the third-order terms in the Hamiltonian of the polar model of an atomic semiconductor determine the probabilities of different processes of transformation of certain quasi-particles into others. Furthermore, the theory permits us to calculate the probability of formation of excitons under the action of incident light. This gives the probability, knowing the matrix elements of the corresponding transitions, of writing down the kinetic equations[6], but in the present work the interaction of quasi-particles with phonons will not be considered. Moreover, this interaction is essential for the study of kinetics in semiconductors, since without consideration of the recombination of holes and doublets with radiation of phonons it is impossible to obtain reasonable equations of kinetics, leading to a correct value of the number of quasi-particles in stationary states. Therefore, the equations of macrokineties for holes and doublets are supplemented by phenomenological terms taking into account the thermal recombination of holes and doublets.

It is postulated that the energy of excitation of excitons is much larger than the excitation energy of holes and doublets; thus in the first approximation it is possible to assume that, in contrast with doublets and holes, thermal excitons do not exist.

The equations of macrokinetics have the form

$$dM'/dt = \lambda Q - 2\gamma M_0 M', \tag{7.1}$$

$$dL'/dt = \lambda Q - 2\gamma M_0 L',$$

$$dQ/dt = 2w_0 n_\alpha + (w_0 + \lambda) Q,$$

where M' is the number of L', photo-holes of photo-doublets, Q of excitons (right- and left-hand), M_0 of thermal holes, γ the recombination coefficient of holes and doublets, n_α the number of photons, w_0 the absorption coefficient of a photon, λ the coefficient of the probability of decay of an exciton into a doublet and a hole (at an impurity atom or spontaneously).

Solving the system of Eqs. (7.1) we obtain

$$M' = M'_{\text{stat}}\left[1 + \frac{e^{-(w_0+\lambda)t}}{(w_0+\lambda)/2\gamma M_0 - 1} + \frac{e^{-2\gamma M_0 t}}{2\gamma M_0/(w_0+\lambda) - 1}\right], \tag{7.2}$$

$$L' = M', \quad Q = Q_{\text{stat}}[1 - e^{-(w_0+\lambda)t}],$$

$$M'_{\text{stat}} = w_0 n_\alpha \lambda / \gamma M_0 (w_0 + \lambda); \tag{7.3}$$

$$Q_{\text{stat}} = 2w_0 n_\alpha / (w_0 + \lambda).$$

The dependence on temperature enters only into M_0, $M_0 \sim e^{-\Delta E/2kT}$, where ΔE is the energy gap between the currentless states of the crystal and the conduction band. From (7.2) it follows that the number of excitons in the crystal, as one was led to expect, does not depend on temperature. As regards the kinetics of photo-holes, the following limiting cases can occur:

a) $w_0 + \lambda \gg 2\gamma M_0,$ (7.4)

then $M' = M'_{\text{stat}}(1 - e^{-2\gamma M_0 t}),$

b) $w_0 + \lambda \ll 2\gamma M_0,$ (7.5)

then $M' = M'_{\text{stat}}(1 - e^{-(w_0+\lambda)t}).$

With increasing temperature the number of thermal holes M_0 increases and, consequently, the thermal conductivity increases, while the stationary value of the photoconductivity will decrease with increase of temperature,

$$\Delta\sigma_{\text{stat}} \sim e^{\Delta E/2kT}. \tag{7.6}$$

This results from the fact that with the increase of temperature the recombination of photo-holes with doublets (and photo-doublets with holes) proceeds more intensively.

As was shown by Zhuze and Ryvkin[7], the stationary concentration of carriers of photocurrent can be represented in the form of a product of a set of parameters

$$\Delta n_{\text{stat}} = \tau k \beta I, \tag{7.7}$$

where τ is the lifetime of the carriers of photocurrent, k the coefficient of absorption, I the intensity of the light, and β the coefficient of the photoeffect which, if I is measured by the number of quanta falling per second on a unit surface area, has the sense of the "quantum yield".

The photoconductivity is determined by the formula

$$\Delta\sigma_{\text{stat}} = eu\Delta u_{\text{stat}}, \tag{7.8}$$

where e is the electronic charge, u is the mobility of the carriers of photocurrent. The number of quanta absorbed per second in a unit volume is equal to $kI = 2w_0 n_\alpha$; therefore,

$$\Delta n_{\text{stat}} = M'_{\text{stat}} = 2\beta\tau w_0 n_\alpha. \tag{7.9}$$

From Eqs. (7.3) and (7.9) we obtain for the quantum yield

$$\beta = \lambda / 2\gamma\tau M_0 (w_0 + \lambda). \tag{7.10}$$

Let us consider two limiting cases:

a) $w_0 + \lambda \gg 2\gamma M_0$, then from (7.4) and (7.10) we have

$$\tau = 1/(2\gamma M_0), \quad \beta = \lambda / (w_0 + \lambda);$$

b) $w_0 + \lambda \ll 2\gamma M_0$, then from (7.5) and (7.10) we have

$$\tau = 1/(w_0 + \lambda), \quad \beta = \lambda / 2\gamma M_0.$$

Let us now write out the temperature dependence of $\Delta\sigma_{\text{stat}}$, τ, and β in both limiting cases:

$$\text{a) } \Delta\sigma_{\text{stat}} \sim e^{\Delta E/2kT},\ \tau \sim e^{\Delta E/2kT},\ \beta \sim \text{const};$$
$$\text{b) } \Delta\sigma_{\text{stat}} \sim e^{\Delta E/2kT},\ \tau \sim \text{const},\ \beta \sim e^{\Delta E/2kT}$$

All the reasoning carried out up to this time is valid for sufficiently high temperatures ($M' \ll M_0$). As regards the region of low temperatures, here it is already impossible to assume $M' \ll M_0$. This introduces changes into the kinetic equations. In particular, the first of the Eqs. (7.1) ceases to be linear and takes the form

$$dM'/dt = \lambda Q - 2\gamma M_0 M' - \gamma M'^2. \qquad (7.11)$$

The solution of this equation can be expressed in Bessel functions of order

$$p = \frac{2}{w_0 + \lambda}\left[\gamma^2 M_0^2 + 2\gamma\,\frac{w_0 n_\alpha + \lambda}{w_0 + \lambda}\right]^{1/2}.$$

Naturally it is difficult to say anything definite about the behavior of the solution; therefore, in the case of low temperatures, we have limited ourselves to finding the stationary value of M'. In this case

$$M'_{\text{stat}} = [2w_0 n_\alpha \lambda / \gamma(w_0 + \lambda)]^{1/2} = \text{const}. \qquad (7.12)$$

Since $M'_{\text{stat}} \sim \Delta\sigma_{\text{stat}}$, we obtained the result that at low temperatures the stationary photoconductivity does not depend on the temperature.

For the limiting case b) we know no experimental data supporting the temperature variation of τ and β in this case. It is possible that this case is not realized.

If one compares the temperature variation of $\Delta\sigma_{\text{stat}}$, τ and β in case a) with experimental data for copper oxide, obtained by Zhuze and Ryvkin[8], in the region of sufficiently high temperatures ($T > -40°$) one gets complete agreement with the temperature variation of $\Delta\sigma_{\text{stat}}$, τ and β obtained experimentally. As regards the region of low temperatures, the temperature variation of $\Delta\sigma_{\text{stat}}$ agrees well with the experimental data. To say anything definite about the temperature variation of the lifetime τ and the quantum yield β in the case of low temperatures is hardly possible; but since the predictions of the present theory differ from those of the theory of Zhuze and Ryvkin, it is hardly possible to obtain the same temperature dependence for τ and β as obtained by them. In the first place, these authors consider that the photoconductivity remains linear even at low temperatures; in the second place, they consider that the decay of an exciton takes place at defects, in which are found electrons removed from the normal band, whereby upon the decay of an exciton the electron is thrown back from the defect to the conduction band[9]. Thus the number of "effective" decay centers depends on the temperature, and their states does not change upon the decay of an exciton (empty sites). Apparently this difference must lead to another temperature dependence of the quantum yield in the region of low temperatures.

We must also mention that copper oxide does not belong to the atomic semiconductors which are considered in the present theory; however, it is entirely possible that the dependences proposed by Zhuze and Ryvkin are of general character.

Therefore, at sufficiently high temperatures, the expression for the stationary photoconductivity created by holes has the form

$$\Delta\sigma_{\text{stat}} = \lambda e\,ukI / 2\gamma M_0(w_0 + \lambda). \qquad (7.13)$$

At low temperatures the formula

$$\Delta\sigma_{\text{stat}} = (\lambda kI)^{1/2} eu / \gamma^{1/2}(w_0 + \lambda)^{1/2} \qquad (7.14)$$

holds.

Analogous expressions can also be written down for the photoconductivity caused by doublets. However, the hole photocurrent can have a different value from that of the doublet photocurrent, if there is a different mobility for doublets and for holes.

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Translated by C. W. Helstrom
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