

*SPIN ORIENTATION OF ELECTRONS ASSOCIATED WITH THE INTERBAND  
ABSORPTION OF LIGHT IN SEMICONDUCTORS*

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The dependence of the degree of orientation of the electrons, which are excited into the conduction band by circularly polarized light, on the frequency of the light is investigated theoretically. It is shown that this dependence has a sharp bend at the absorption threshold connected with the presence of the split-off valence sub-band. The spin relaxation of the electrons in crystals without an inversion center, caused by the spin splitting of the conduction band, is considered. In the case of rapid spin relaxation, the steady-state orientation of the electrons may vanish even before the absorption threshold connected with the split-off sub-band is reached. In this connection, after the threshold is reached the spin orientation must appear again, but its sign is opposite to the sign it had before threshold. The polarization of the radiation which arises upon recombination of the oriented electrons with holes is considered.

### 1. INTRODUCTION

THE optical orientation of gas atoms has been well investigated and has been found to be an extremely effective means of investigating atomic processes.<sup>[1]</sup> Recently the first successful experiments were carried out on the optical orientation of the free electrons in semiconductors.<sup>[2-5]</sup> In these experiments the interband absorption of circularly polarized light led to the creation of an appreciable spin orientation of the electrons in the conduction band. The orientation was detected by measuring the nuclear magnetization which arises as a result of the Overhauser effect<sup>[2]</sup> or from the polarization of the luminescence.<sup>[3-5]</sup>

The possibility of optical orientation connected with the interband transitions in semiconductors with diamond or zinc blende structure can be understood in the following way. If, for example, the top of the valence band belongs to the representation  $\Gamma_8$ , and the bottom of the conduction band belongs to the representation  $\Gamma_6$ , then the selection rules for interband absorption are the same as for an atomic transition between levels with angular momenta  $3/2$  and  $1/2$ . In such a scheme, the following two transitions are possible upon the absorption of left-hand circularly polarized light: the transition from the lower state with magnetic quantum number  $\mu = 3/2$  to the upper state with magnetic quantum number  $m = 1/2$ , and the transition from the state  $\mu = 1/2$  to the state  $m = -1/2$ . Here  $m$  and  $\mu$  denote the components of the angular momentum along the direction of the light beam. The probabilities of these transitions are in the ratio 3:1, so as a consequence three times as many electrons with their spins oriented along the light beam are excited into the conduction band, as compared to the number of electrons with oppositely directed spin. This corresponds to the degree of orientation  $P_0 = 1/2$ . A left-hand circularly polarized photon has the component of its angular momentum along the direction of its linear momentum equal to  $-1$ . This angular momentum is completely transferred to the crystal upon absorption. However, the preferential direction of the spin of an

electron in the conduction band turns out to be opposite to the direction of spin of a photon in the exciting light beam. Correspondingly, the spin of the hole which is created in the valence band is parallel to the photon spin and exceeds it by the amount required by conservation of angular momentum.

In the valence band the spin relaxes rapidly, but the spin relaxation time of the electrons in the conduction band may exceed their lifetime. In this connection the recombination radiation will be circularly polarized with the same kind of circular polarization as the exciting light. Upon recombination with holes, the electrons with spin  $m = 1/2$  give radiation with the degree of circular polarization equal to 50% (upon observation along or against the exciting beam). Electrons with spin  $m = -1/2$  give radiation of the opposite polarization. If spin relaxation is neglected in general, then the resulting degree of circular polarization of the radiation will amount to 25%, since the degree of orientation of the electrons is given by  $P_0 = 1/2$ . Spin relaxation decreases the orientation of the recombination electrons in the ratio  $\tau_S(\tau_S + \tau)^{-1}$  where  $\tau_S$  is the spin relaxation time and  $\tau$  is the lifetime of the electron.

Thus, three processes determine the polarization of the recombination radiation: 1) the creation of oriented electrons by polarized light, 2) spin relaxation which occurs during the lifetime of the electron (we note that in this stage, the effect of even very weak external fields may substantially change the orientation of the electrons), and 3) radiative recombination of the oriented electrons.

The simple considerations discussed above are valid if the energy  $\hbar\omega$  of the exciting photons only slightly exceeds the width  $E_g$  of the forbidden energy gap. As is shown below, with increasing  $\hbar\omega - E_g$ , the degree of orientation of the electrons, and hence the polarization of the luminescence, may change because of the following reasons.

In the first place, in semiconductors in which the spin-orbit splitting  $\Delta$  of the valence band is small, the states of the split-off sub-band begin to be mixed in with the states of the light and heavy holes. Because of this

the relative probabilities for the excitation of electrons with different spins into the conduction band are changed. For  $\hbar\omega - E_g > \Delta$  transitions from the split-off sub-band begin to occur. The appropriate selection rules show that for such transitions electrons whose orientation is  $P_0 = -1$  are excited into the conduction band, i.e., the orientation of the electrons is opposite to that of the electrons which are excited from the sub-bands of the heavy and light holes. Therefore, the resulting degree of orientation must decrease for  $\hbar\omega - E_g > \Delta$ .

Secondly, the spin relaxation of the electrons depends on their energy. As is shown in the present article, in crystals without a center of inversion (for example, in  $A^{III}B^V$  compounds) a strong spin relaxation may occur as a consequence of the splitting of the conduction band, which is connected with the cubic terms in the dependence of the energy on the quasimomentum. The rate of spin relaxation determined by this mechanism increases very rapidly with increasing energy of the electron. Therefore, the orientation may vanish even before  $\hbar\omega - E_g$  reaches the value  $\Delta$ . In this case, an orientation of the opposite sign must appear for  $\hbar\omega - E_g > \Delta$ .

We note that the decrease of the orientation associated with the increase of  $\hbar\omega - E_g$  was observed in articles [3-5].

The dependence of the degree of orientation of the electrons on the intensity of the light is substantially different in p-type and n-type materials. In a p-type material the degree of orientation does not depend on the intensity of the irradiation as long as the concentration of nonequilibrium carriers is small in comparison with the concentration of equilibrium holes. In an n-type material the degree of orientation is proportional to the intensity for small intensities of the light. With an increase of the intensity, the degree of orientation becomes appreciable and saturates at those intensities when the concentration of nonequilibrium carriers is still small in comparison with the concentration of equilibrium electrons. Thus, in an n-type material the optical orientation of the equilibrium carriers may be achieved.<sup>[6]</sup>

## 2. THE CREATION OF ORIENTED ELECTRONS BY POLARIZED LIGHT

The electric field of the light wave acts directly only on the orbital motion of the electron, but not on its spin. Therefore, spin orientation associated with interband absorption can be realized only by means of the spin-orbit interaction. As is well-known, this interaction leads to a splitting of the valence band into the bands of light and heavy holes, whose energies coincide for zero quasimomentum, and the so-called split-off band. In the presence of a center of inversion, each of these three bands is doubly degenerate (Kramers degeneracy).<sup>1)</sup> The top of the split-off band lies below the tops of the light and heavy hole bands by the energy  $\Delta$ , which characterizes the magnitude of the spin-orbit coupling.

<sup>1)</sup>In crystals having the structure of zinc blende, Kramers degeneracy does not occur due to the absence of a center of inversion. The splittings of the valence sub-bands associated with this do not play an essential role. Splitting of the conduction band leads to the important mechanism of spin relaxation which is discussed in Section 3.

The degree of orientation of the conduction electrons, which is created by circularly polarized light, essentially depends on the relation between the quantities  $\hbar\omega - E_g$  and  $\Delta$ , where  $\hbar\omega$  denotes the energy of the light quantum and  $E_g$  is the width of the forbidden energy gap. If  $\hbar\omega - E_g \ll \Delta$ , then those electrons are excited into the conduction band from the valence band for which the spin-orbit coupling is large, and the degree of orientation amounts to 50% (the same as for an atomic transition between levels with spins  $3/2$  and  $1/2$ ). If on the other hand  $\hbar\omega - E_g \gg \Delta$ , then one can neglect the spin-orbit interaction, and the optical orientation of the electrons is absent. In the general case the orientation of the electrons at the moment of creation is characterized by the density matrix

$$F_{mm'} = \frac{2\pi}{\hbar} \int \frac{d^3p}{(2\pi\hbar)^3} \sum_n \delta[\epsilon_c(\mathbf{p}) + \epsilon_{vn}(\mathbf{p}) + E_g - \hbar\omega] \times \sum_\alpha (d_{m, n\alpha} \mathbf{E})(d_{m', n\alpha} \mathbf{E})^* \quad (1)$$

Here the subscripts  $m$  and  $m'$  denote the components of the electron's spin along the direction of propagation of the light and may take the values  $\pm 1/2$ ; the subscript  $n$  labels the three sub-bands of the valence band: the bands of heavy and light holes and the split-off band; the subscript  $\alpha$  labels the two degenerate states inside each of these sub-bands;  $\epsilon_c(\mathbf{p})$  and  $\epsilon_{vn}(\mathbf{p})$  denote the electron's energy in the conduction band and in the  $n$ -th sub-band of the valence band, respectively;  $d_{m, n\alpha}$  denotes the matrix element of the dipole moment operator for the transition;  $\mathbf{E}$  is the complex amplitude of the electric field in the light wave. We assume that the valence band is practically completely filled and the conduction band is empty, that is, the holes and electrons are not degenerate or the quantity  $\hbar\omega - E_g$  is larger than the Fermi energy.

It is convenient to represent  $F_{mm'}$  in the form

$$F_{mm'} = N_0 \delta_{mm'} + \sigma_{mm'} S_0, \quad (2)$$

where  $\sigma$  denotes the Pauli matrices. The quantity  $2N_0 = \text{Trace } F$  gives the total number of electrons per unit volume which are excited into the conduction band per unit time by the light; the vector  $\mathbf{S}_0 = \frac{1}{2} \text{Trace } (F\sigma)$  represents the total spin of these electrons. For a cubic crystal one can write

$$N_0 = K|E|^2, \quad S_0 = -iR[EE^*], \quad (3)^*$$

where  $K$  and  $R$  are certain functions of the light frequency  $\omega$ . It is obvious that the quantity  $K$  is proportional to the absorption coefficient. Having taken the trace of both sides of formula (1), we obtain

$$K = \sum_n K_n, \quad (4)$$

$$K_n = \frac{1}{6} \frac{2\pi}{\hbar} \int \frac{d^3p}{(2\pi\hbar)^3} \delta[\epsilon_c(\mathbf{p}) + \epsilon_{vn}(\mathbf{p}) + E_g - \hbar\omega] \sum_{m\alpha} (d_{m, n\alpha} d_{m, n\alpha}^*).$$

Having calculated  $\text{Trace } F\sigma$ , we obtain the following expression for  $R$ :

$$R = \sum_n R_n, \quad R_n = \frac{i}{12} \frac{2\pi}{\hbar} \int \frac{d^3p}{(2\pi\hbar)^3} \delta[\epsilon_c(\mathbf{p}) + \epsilon_{vn}(\mathbf{p}) + E_g - \hbar\omega] \times \sum_{mm'\alpha} (\sigma_{mm'} [d_{m, n\alpha} d_{m', n\alpha}^*]). \quad (5)$$

\*[EE\*]  $\equiv E \times E^*$ .

In formulas (4) and (5) we have represented the quantities  $K$  and  $R$  in the form of a sum of the contributions from each of the valence sub-bands separately.

In order to calculate  $K_n$  and  $R_n$  we choose as the basis functions in the valence band the functions  $u_{j\mu}$ ,<sup>[7]</sup> where  $j = \frac{1}{2}$  and  $\frac{3}{2}$  label the irreducible representations  $\Gamma_7$  and  $\Gamma_8$  of the cubic group, respectively. Then the wave functions  $\psi_{n\alpha p}$  of an electron in the valence band have the form

$$\psi_{n\alpha p} = \sum_{j\mu} \chi_{n\alpha}^{j\mu}(\mathbf{p}) u_{j\mu}. \quad (6)$$

For the subsequent discussion, the following property of the functions  $\chi_{n\alpha}^{j\mu}(\mathbf{p})$  is essential, where this property follows from group-theoretic considerations:

$$\sum_{\alpha} \int d^3p \chi_{n\alpha}^{j\mu}(\mathbf{p}) \chi_{n\alpha}^{j'\mu'}(\mathbf{p}) Q(\mathbf{p}) = 2 \frac{\delta_{j\mu} \delta_{j'\mu'}}{2j+1} \int d^3p |a_n^{j\mu}(\mathbf{p})|^2 Q(\mathbf{p}), \quad (7)$$

where  $Q(\mathbf{p})$  denotes any invariant of the cubic group. Here the notation

$$|a_n^{j\mu}(\mathbf{p})|^2 = \frac{1}{2} \sum_{\mu'} |\chi_{n\alpha}^{j\mu}(\mathbf{p})|^2. \quad (8)$$

has been introduced. Formula (7) follows from the fact that the expression  $\sum_{\alpha} \chi_{n\alpha}^{j\mu}(\mathbf{p}) \chi_{n\alpha}^{j'\mu'}(\mathbf{p})$  transforms according to the direct product of the irreducible representations  $j$  and  $j'$ . We note that on account of the normalization of the functions (6) the relation

$$\sum_j |a_n^{j\mu}(\mathbf{p})|^2 = 1. \quad (9)$$

is satisfied.

Calculating the matrix elements  $d_{m,n\alpha}$  with the aid of the functions (6) and using the property (7), from formulas (4) and (5) we obtain

$$K_n = D \int \frac{d^3p}{(2\pi\hbar)^3} \delta[\varepsilon_c(\mathbf{p}) + \varepsilon_{vn}(\mathbf{p}) + E_g - \hbar\omega], \quad (10)$$

$$R_n = \frac{D}{2} \int \frac{d^3p}{(2\pi\hbar)^3} \delta[\varepsilon_c(\mathbf{p}) + \varepsilon_{vn}(\mathbf{p}) + E_g - \hbar\omega] \quad (11)$$

$$[|a_n^{1/2}(\mathbf{p})|^2 - 2|a_n^{3/2}(\mathbf{p})|^2].$$

Here the constant  $D = 2\pi(S|d_Z|Z)^2(3\hbar)^{-1}$  has been introduced, where  $(S|d_Z|Z)$  denotes the interband matrix element of the dipole moment.

According to formulas (2) and (3) the initial degree of orientation of the electrons which are excited by circularly polarized light from the valence sub-band  $n$  into the conduction band is given by<sup>2)</sup>

$$P_0^{(n)} = R_n/K_n. \quad (12)$$

The degree of orientation  $P_0$  of all of the electrons which are excited into the conduction band is determined by the formula

$$P_0 = \sum_n R_n / \sum_n K_n = \sum_n P_0^{(n)} K_n / \sum_n K_n. \quad (13)$$

<sup>2)</sup>The degree of orientation  $P_0$  is defined so that it is positive if the spin of the electrons is directed opposite to the spin of the exciting photons (i.e., opposite to the vector  $\mathbf{i} \mathbf{E} \times \mathbf{E}^*$ ). In other words,  $P_0 > 0$  if upon excitation by left-hand circularly polarized light the spin of the electrons is oriented along the direction of propagation of the light.

In what follows we shall assume that the values  $n = 1, 2, 3$  pertain, respectively, to the bands of heavy and light holes and to the split-off band. If  $\hbar\omega - E_g \ll \Delta$ , then the split-off band does not give any contribution to the absorption ( $K_3 = R_3 = 0$ ), and for the light and heavy hole bands  $a_1^{1/2} = a_2^{1/2} = 0$  so that according to Eq. (9)  $|a_1^{3/2}| = |a_2^{3/2}| = 1$ . In this connection, from formulas (10)–(13) we obtain  $P_0^{(1)} = P_0^{(2)} = P_0 = \frac{1}{2}$ .

Thus, at the fundamental absorption edge the bands of heavy and light holes give an identical degree of orientation of the electrons—namely, 50%. We emphasize that this result does not depend on the degree of corrugation of the constant energy surfaces or on the direction of propagation of the exciting light wave with respect to the crystal axes.

Now let us find the dependence of the degree of orientation on the frequency  $\omega$ . As before we shall assume that  $\hbar\omega - E_g \ll E_g$ ; by the same token our calculations relate to the case when  $E_g \gg \Delta$ . (Such a relation holds, for example, for gallium arsenide.)

The wave functions and the spectrum in the valence band for this case were found by Kane.<sup>[8]</sup> For our purposes it is convenient to start from the Hamiltonian, written down according to the method of Luttinger,<sup>[9]</sup>

$$H = -(A + 2B)p^2 + 3B(\mathbf{pL})^2 - \frac{2}{3}\Delta(\sigma L) + \frac{1}{3}\Delta. \quad (14)$$

The Hamiltonian  $H$  is represented by a  $6 \times 6$  matrix;  $L_x, L_y, L_z$  denote the matrices for orbital angular momentum  $l = 1$ ;  $\sigma_x, \sigma_y, \sigma_z$  are Pauli matrices. The constants in the Hamiltonian are chosen so that  $A, B$ , and  $\Delta$  coincide with the constants specifying the energy spectrum in Kittel's book.<sup>[7]</sup> The energy is measured downwards from the tops of the bands of the heavy and light holes. We note that usually  $A < 0, B < 0$ , and  $\Delta > 0$ .

In order to simplify the calculations, the terms in the Hamiltonian (14) which are responsible for the undulation of the energy surfaces are not taken into account. Since the degree of orientation is determined by quantities which are averaged over the direction of the quasimomentum, taking the undulations into account cannot substantially affect the results.

The spherical symmetry of the Hamiltonian (14) permits us to seek its eigenfunctions in the form

$$\chi^{\mu}(\mathbf{p}) = a^j(\mathbf{p}) D_{\mu, j}^j(\varphi, \theta, \psi), \quad (15)$$

where  $\varphi$  and  $\theta$  denote the polar angles of the vector  $\mathbf{p}$  in a certain fixed coordinate system,  $\psi$  is an arbitrary angle determining the choice of the phase of the wave function (one can, for example, put  $\psi = 0$ ), and  $D_{\mu, M}^j(\varphi, \theta, \psi)$  are the matrices characterizing finite rotations,<sup>[10]</sup> where the subscript  $M$  may take the values  $\pm \frac{3}{2}, \pm \frac{1}{2}$ . Having substituted (15) into the equation  $H\psi = E\psi$ , we obtain the following equation for the coefficients  $a^j$ :

$$\begin{aligned} &\{-(A + 2B)p^2 - \frac{1}{3}\Delta[j(j+1) - \frac{1}{3}j^2]\} a^j \\ &+ 3Bp^2 \sum_{j'} (jM|L_z^2|j'M) a^{j'} = E a^j. \end{aligned} \quad (16)$$

Setting  $M = \pm \frac{3}{2}$ , let us find the spectrum and wave function of the heavy holes:

$$\varepsilon_{\text{eh}} = (B - A)p^2, \quad |a_1^{3/2}| = 1, \quad a_1^{1/2} = 0. \quad (17)$$

For  $M = \pm \frac{1}{2}$  we obtain the following system of equations:

$$\begin{aligned} -(A+B)p^2 a^{1/2} \pm B\sqrt{2}p^2 a^{1/2} &= E a^{1/2}, \\ \pm B\sqrt{2}p^2 a^{1/2} - (A p^2 - \Delta) a^{1/2} &= E a^{1/2}. \end{aligned} \quad (18)$$

From here we find the spectrum of the light holes

$$\epsilon_{sc} = -(A+B/2)p^2 + \frac{1}{2}\Delta - \frac{1}{2}(9B^2p^4 + 2B\Delta p^2 + \Delta^2)^{1/2} \quad (19)$$

and the spectrum of the split-off band

$$\epsilon_{so} = -(A+B/2)p^2 + \frac{1}{2}\Delta + \frac{1}{2}(9B^2p^4 + 2B\Delta p^2 + \Delta^2)^{1/2}. \quad (20)$$

The value of the coefficients  $a_{2,3}^{3/2}$  and  $a_{2,3}^{1/2}$  for each of the sub-bands is determined by Eqs. (18) and by the normalization condition  $|a_n^{3/2}|^2 + |a_n^{1/2}|^2 = 1$ . In this connection, the two signs in Eqs. (18) correspond to the two degenerate states inside each of the sub-bands.

We recall that we are considering the range of energies  $\epsilon \ll E_g$  and we assume that  $\Delta \ll E_g$ . The cited results, of course, coincide with Kane's results<sup>[8]</sup> for this case. Neglect of the corrugation of the energy surfaces has made it possible to derive the spectrum and the wave functions in explicit form.

Using formulas (10)–(12) and expressions (17)–(20), we obtain the following results for the partial degrees of orientation:

$$P_0^{(1)} = \frac{1}{2}, \quad P_0^{(2,3)} = \frac{(1+\beta)(\mp g - 6x + 9\beta - 5)}{4(\pm\beta g + 6x - \beta - 3)}. \quad (21)$$

Here the following notation has been introduced:

$$\beta = -\frac{2}{3B} \left( \frac{\hbar^2}{2m_c} - A - \frac{B}{2} \right), \quad (22)$$

$$g = [36x^2 - 12x(\beta + 3) + (3\beta + 4)^2]^{1/2}, \quad (23)$$

$$x = (\hbar\omega - E_g) / \Delta.$$

In formula (21) the upper sign associated with  $g$  corresponds to the band of light holes, and the lower sign corresponds to the split-off band. The parameter  $\beta$  can be expressed in terms of the mass  $m_h$  of the heavy holes, the mass  $m_l$  of the light holes, and the electron mass  $m_c$  in the conduction band:

$$\beta = \frac{4}{3} \frac{m_c^{-1} + 3m_l^{-1/4} + m_h^{-1/4}}{m_l^{-1} - m_h^{-1}}. \quad (24)$$

Computation of the quantities  $K_n$ , which are proportional to the coefficients of absorption from the  $n$ -th valence sub-band, gives

$$K_1 = D' \sqrt{2x} (3\beta - 3)^{-1/2}, \quad (25)$$

$$K_{2,3} = D' k \frac{2x - 3\beta k^2 - 1}{3\beta(2x - 3\beta k^2 - 1) + 9k^2 - 1}, \quad (26)$$

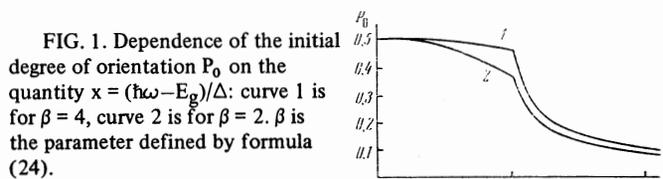
where  $D'$  is a certain constant,

$$k^2 = (\pm g + 6\beta x - 3\beta - 4) [9(\beta^2 - 1)]^{-1}, \quad (27)$$

and where, as before, the upper sign refers to the band of light holes and the lower sign refers to the split-off band.

As is clear from formulas (13) and (21)–(27), the dependence of the degree of orientation on the frequency of the light is determined by only the single parameter  $\beta$ . For gallium arsenide  $\beta \approx 4$ .

The degree of orientation  $P_0^{(1)} = \frac{1}{2}$ , independently of the frequency of the light,  $P_0^{(2)}$  varies from the value  $\frac{1}{2}$  at the absorption threshold to the value  $-\frac{1}{2}$  for large



values of  $x$ , and  $P_0^{(3)}$  varies from the value  $-1$  for  $x = 1$  to zero.

The resulting degree of orientation  $P_0$  as a function of the frequency of the light is shown in Fig. 1. The most interesting property of this dependence is the sharp kink at  $\hbar\omega - E_g = \Delta$  ( $x = 1$ ) at the threshold for the absorption associated with the split-off band. This kink is caused by the fact that the orientation of the electrons, which are excited into the conduction band from the split-off band, is opposite to the orientation which exists for  $x < 1$ , and the number of such electrons rapidly increases (like  $\sqrt{x-1}$ ). Upon a reduction of  $\beta$ , the decrease in the degree of orientation after the kink becomes less pronounced. For larger values of  $\beta$  the degree of orientation does not depend on  $\beta$  and is described by the simple formulas

$$P_0(x) = \frac{1}{2} \text{ for } x < 1, \\ P_0(x) = \frac{\sqrt{x-1}}{2\sqrt{x} + \sqrt{x-1}} \text{ for } x > 1. \quad (28)$$

A more exact expression for larger values of  $\beta$  and for  $x < 1$  has the form

$$P_0(x) = \frac{1}{2} - \frac{2}{3} \frac{x^2}{\beta^2}. \quad (29)$$

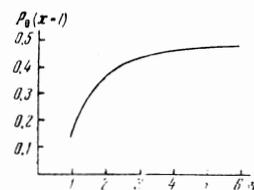
The dependence of the degree of orientation on the parameter  $\beta$  at the point of the kink,  $x = 1$ , is shown in Fig. 2.

### 3. SPIN ORIENTATION OF THE ELECTRONS ASSOCIATED WITH STEADY-STATE EXCITATION

The quantity  $P_0$  calculated above corresponds to the degree of orientation of the electrons at the instant of excitation. The degree of orientation  $P$  sustained under steady-state excitation will generally be smaller than  $P_0$  because of spin relaxation. The rate of spin relaxation depends on the energy of the electron in the conduction band. If the energy of a quantum  $\hbar\omega$  exceeds the width of the forbidden gap  $E_g$  by an amount larger than  $kT$ , then the orientation of the electrons may be already partially lost during the time of their thermalization. This leads to the result that the steady-state degree of orientation  $P$  will depend on the frequency of the exciting light in some other way than  $P_0$  does.

In crystals without a center of inversion there is an effective mechanism of spin relaxation, determined by

FIG. 2. The dependence of the degree of orientation  $P_0$  on the parameter  $\beta$ , defined by formula (24), at the threshold for the absorption connected with the split-off valence sub-band ( $x = 1$ ).



the band structure itself, whose role rapidly increases with increasing electron energy. As is well known,<sup>[7]</sup> in such crystals there is a spin splitting of the conduction band so that the electron's energy depends on the component of its spin in the direction of the vector  $\kappa$  which is related to the momentum ( $\kappa_x = p_x(p_y^2 - p_z^2)$ ,  $\kappa_y = p_y(p_z^2 - p_x^2)$ , and  $\kappa_z = p_z(p_x^2 - p_y^2)$ ). One can write the energy splitting in the form

$$\hbar\Omega = 2\alpha\kappa(2m_e)^{-1/2}E_g^{-1/2}, \quad (30)$$

where  $\alpha$  is a certain numerical coefficient. One can consider the quantity  $\Omega$  as the frequency of precession of the spin in a certain effective magnetic field directed along  $\kappa$ . From formula (30) it is seen that the magnitude of this field is proportional to the cube of the quasimomentum.

If at the initial instant the electron spin makes a certain angle with the vector  $\kappa$ , then subsequently precession of the spin around  $\kappa$  will occur with a frequency  $\Omega$ . The change of the electron momentum upon scattering leads to a rotation of the axis of precession. Thus, the originally existing orientation of the spin will relax. The value of the parameter  $\Omega\tau_p$  (where  $\tau_p$  is the momentum relaxation time) is essential for an estimate of the relaxation rate, where this parameter has the significance of the angle of rotation of the precessing spin between two collisions. If the electron energy is so large that  $\Omega\tau_p \gg 1$ , then the component of the spin perpendicular to  $\kappa$  is lost during a time interval  $\sim \Omega^{-1}$ , and then the remaining orientation relaxes with a characteristic time  $\tau_p$ . If the energy relaxation time  $\tau_\epsilon$  is much larger than  $\tau_p$ , then during the time of thermalization the orientation will be practically completely lost. In the opposite limiting case,  $\Omega\tau_p \ll 1$ , the spin relaxation will be strongly retarded because of the frequent rotations of the axis of precession. In this case the spin relaxation time can be estimated in the following way. The average value  $\overline{\varphi^2}$  of the square of the angle of rotation of the spin during a time interval  $t \gg \tau_p$  can be written in the form  $\overline{\varphi^2} = (\Omega\tau_p)^2 t/\tau_p$ , since  $t/\tau_p$  gives the number of flips of the axis of precession during the time  $t$  and  $\Omega\tau_p$  is the angle of rotation of the spin during the time interval between two such flips. Let us determine the time  $\tau_S$  from the condition  $\overline{\varphi^2} \sim 1$  for  $t = \tau_S$ , from which it follows that

$$\tau_S^{-1} = a\overline{\Omega^2}\tau_p, \quad \overline{\Omega^2} = \frac{16}{35}a^2\epsilon^3/\hbar^2E_g, \quad (31)$$

where  $\overline{\Omega^2}$  denotes the value of  $\Omega^2$  averaged over angles, and  $a$  is a certain numerical coefficient which depends on the mechanism of momentum relaxation. For example,  $a = 1/9$  for the relaxation due to Coulomb collisions, as a rigorous calculation shows. The retardation of the spin relaxation due to the frequent collisions which change the momentum is analogous to the dynamic narrowing of a magnetic resonance line.<sup>[11]</sup>

Now let us consider an electron with initial energy  $\epsilon_0$  and orientation  $P_0$ . Let us denote the degree of orientation of this electron after its thermalization by  $P_T$ . Then

$$P_T = P_0 \exp(-\Phi), \quad \Phi = \int_0^t \frac{dt}{\tau} = \int_0^{\epsilon_0} \frac{d\epsilon}{\epsilon_s} \frac{\tau_\epsilon}{\tau_s}, \quad (32)$$

where  $\tau_\epsilon$  is the energy relaxation time, and  $t$  is the time required for thermalization, which is assumed to be

much smaller than the lifetime. Assuming that  $\tau_\epsilon/\tau_S$  is proportional to  $\epsilon^\nu$ , we obtain  $\Phi = \nu^{-1}(\tau_\epsilon/\tau_S)_{\epsilon=\epsilon_0}$ . Substituting expression (31) for  $\tau_S$  here, we find

$$\Phi = a\nu^{-1}(\overline{\Omega^2}\tau_p\tau_\epsilon)_{\epsilon=\epsilon_0}. \quad (33)$$

The factor  $\exp(-\Phi)$  which appears in formula (32) depends very strongly on the initial electron energy  $\epsilon_0$ . For example, if the electron loses momentum during scattering by ionized impurities and holes, but it loses energy upon scattering by holes (in p-type material), then  $\tau_p$  and  $\tau_\epsilon$  are proportional to  $\epsilon^{3/2}$ . Since  $\overline{\Omega^2} \sim \epsilon^3$ , then in this case  $\Phi \sim \epsilon_0^6$ . Estimates show that in p-type GaAs with a hole concentration of the order of  $10^{19} \text{ cm}^{-3}$  the critical energy, at which the quantity  $\Phi$  becomes of the order of unity, amounts to several tenths of an electron volt. Under such conditions Zakharchenya, Fleisher et al.<sup>[6]</sup> observed a dependence of the polarization of the radiation on the frequency of the exciting light which is qualitatively in agreement with Fig. 1. With a decrease in the impurity concentration  $N$  the critical energy falls off like  $N^{1/3}$ ; therefore, in purer samples one can expect the orientation of the electrons to already vanish for values of  $\hbar\omega - E_g$  which are smaller than the spin-orbit splitting  $\Delta$ . The decrease of the critical energy associated with the decrease of the impurity concentration will, however, be limited by scattering by polar optical lattice vibrations.

Let us emphasize the unusual nature of the situation: the stronger the relaxation of the electrons in energy and momentum, the weaker the spin relaxation.

Now let us present the formula for the degree of orientation  $P$  of the electrons upon steady-state excitation:

$$P = \frac{\sum_n P_T^{(n)} K_n}{\sum_n K} \frac{\tau_{\tau\tau}}{\tau_{\tau\tau} + \tau}, \quad P_T^{(n)} = P_0^{(n)} \exp(-\Phi_n), \quad (34)$$

where  $\Phi_n$  is determined by formula (33) in which  $\epsilon_0$  denotes the initial energy of the electron excited into the conduction band from the  $n$ -th valence sub-band, and  $\tau$  and  $\tau_{ST}$  respectively denote the lifetime and the spin relaxation time of the thermalized electrons.

Formula (34) reflects the following model for the establishment of a steady-state orientation. The electrons, which are excited out of the  $n$ -th valence sub-band into the conduction band, have an initial degree of orientation  $P_0^{(n)}$ , which decreases to the value  $P_T^{(n)}$  during the process of thermalization. It is assumed that the time required for thermalization is much smaller than the lifetime. The second factor in formula (34) takes the spin relaxation of the thermalized electrons into account.

We note that the thermalization process may consist of two stages: a rapid cooling to an energy  $\epsilon < \hbar\omega_L$  because of the emission of optical phonons with energy  $\hbar\omega_L$  and then, more slowly, a relaxation to thermal energies. Under these conditions the quantity  $\Phi$  will be an oscillating function of the initial energy  $\epsilon_0$  of the electron (with period  $\hbar\omega_L$ ), since the contribution of the second stage of thermalization to  $\Phi$  depends on  $\epsilon_0 - n\hbar\omega_L$ . Here  $n$  is the maximum number of optical phonons which can be emitted by an electron with energy  $\epsilon_0$ . The oscillations of the degree of orientation may be extremely deep in view of the exponential de-

pendence of  $P_T$  on  $\Phi$ . Such oscillations were experimentally observed in GaSb by Parsons.<sup>[3]</sup>

However, for  $\epsilon_0 \approx \Delta$  the quantity  $\exp(-\Phi)$  is already small, so with an increase of the frequency  $\omega$  of the exciting light the degree of orientation falls off substantially even before reaching the absorption threshold connected with the split-off valence sub-band. After reaching this threshold, the electrons which are excited from the split-off sub-band to the bottom of the conduction band will give the major contribution to the orientation, so that an orientation of the electrons again appears for  $\hbar\omega - E_g > \Delta$ . The sign of this orientation is opposite to the sign of the orientation which existed for  $\hbar\omega - E_g < \Delta$ , since  $P_0^{(s)} = -1$  at the threshold for the absorption connected with the split-off sub-band. In the limiting case when  $\beta \gg 1$  ( $\beta$  is the parameter defined by formula (24)), the dependence of the steady-state degree of orientation on the frequency of the exciting light is given by the following formulas, which are generalizations of formulas (28):

$$P = \frac{1}{2} \frac{\tau_{rr}}{\tau_{rr} + \tau} \exp[-\Phi(\epsilon)] \quad \text{for } \epsilon < \Delta, \quad (35)$$

$$P = \frac{\tau_{rr}}{\tau_{rr} + \tau} \frac{\sqrt{\epsilon} \exp[-\Phi(\epsilon)] - \sqrt{\epsilon - \Delta} \exp[-\Phi(\epsilon - \Delta)]}{2\sqrt{\epsilon} + \sqrt{\epsilon - \Delta}} \quad \text{for } \epsilon > \Delta,$$

where  $\epsilon = \hbar\omega - E_g$ .

#### 4. POLARIZATION OF THE RECOMBINATION RADIATION

According to the correspondence principle, one can regard the spontaneous emission as the radiation of a classical dipole with a dipole moment which coincides with the matrix element of the corresponding transition. Thus, for the square of the q-th component of the radiating dipole one can write down the expression

$$(d^q)^2 = \sum_{ab} f_{ab} d_{b,0} d_{0,a}, \quad (36)$$

where the subscripts a and b denote the set of quantum numbers characterizing the state of the electron-hole system before recombination and the subscript 0 denotes the state which appears after recombination;  $f_{ab}$  denotes the density matrix before recombination.

The degree of circular polarization  $\mathcal{P}$  can be expressed in terms of the quantities  $(d^q)^2$  in the following way:

$$\mathcal{P} = \frac{(d^+)^2 - (d^-)^2}{(d^+)^2 + (d^-)^2}. \quad (37)$$

In what follows we shall consider the recombination of electrons with energy  $\epsilon \ll \Delta$  with heavy and light holes.

In the region where the effective-mass approximation is valid, one can expand the state a (or b) in wave functions which describe the electron (with spin component m) at the bottom of the conduction band and the hole (with spin component  $\mu$ ) at the top of the valence band. Then, after summing over a and b, one can write formula (36) in the following manner:

$$(d^q)^2 = \sum_{mm'\mu\mu'} \Phi_{m\mu, m'\mu'} d_{m,0}^q d_{0,\mu'}^q. \quad (38)$$

The matrix  $\hat{\Phi}$  is the spin density matrix of the electron-hole system. If the spin relaxation time of the electron is considerably greater than the spin relaxation time of the hole, then one can assume that  $\Phi_{m\mu, m'\mu'} = f_{mm'} \delta_{\mu\mu'}$ . Let us represent the density matrix of the electron's spin in the form

$$f_{mm'} = N \delta_{mm'} + \sigma_{mm'} S_z. \quad (39)$$

Then we have

$$(d^q)^2 = AN + qBS_z, \quad q = \pm 1, \quad (40)$$

where

$$A = \sum_{m\mu} |d_{m\mu}^q|^2, \quad B = \sum_{mm'\mu} \sigma_{mm'}^z d_{m\mu}^+ d_{m'\mu}^+. \quad (41)$$

In formula (40)  $S_z$  denotes the component of the electrons' spin in the direction of observation. Only this component influences the radiation. According to formulas (37) and (40), the degree of polarization is expressed in terms of A and B in the following way:

$$\mathcal{P} = \frac{B}{A} |P| \cos \theta,$$

where  $|P| = |\mathbf{S}|/N$  denotes the degree of orientation of the electrons, and  $\theta$  is the angle between the direction of their spin and the direction of observation. Having chosen the dependence of the matrix elements  $d_{m\mu}^q$  on m,  $\mu$ , and q in the usual manner,<sup>[10]</sup> we obtain  $B/A = -1/2$ , so that

$$\mathcal{P} = -1/2 |P| \cos \theta. \quad (42)$$

The minus sign in this formula means that light, which is emitted in the direction of the electron spin, is left-hand circularly polarized. (We note that for the recombination of electrons with holes in the split-off band,  $B/A = +1$  at the top of this band.)

The derivation of formula (42) given above was based only on the effective-mass approximation and on the assumption about the rapid relaxation of the hole's spin. Therefore, this formula is valid both for the recombination of free electrons and holes and also for cases involving band-shallow acceptor and shallow donor-band recombinations.

The polarization of exciton luminescence requires special investigation. In its ground state the exciton may have a total angular momentum  $J = 1$  or  $J = 2$ . Due to the exchange interaction these states have different energies. The polarization of the luminescence substantially depends on the relation between the exchange-splitting energy  $E$  and  $\hbar/\tau_h$ , where  $\tau_h$  denotes the relaxation time of the hole's spin. If  $E \gg \hbar/\tau_h$ , then the coupling between the spins of the electron and hole is strong and relaxation of the hole's spin also leads to relaxation of the electron's spin with the same relaxation time  $\tau_h$ . In this case the exciton luminescence will essentially not be polarized. (We assume that  $\tau_h$  is much smaller than the lifetime of the exciton.) In the opposite case,  $E \ll \hbar/\tau_h$ , the electron's spin is not able to respond to the frequent deflections of the hole's spin. In this connection, the polarization of the radiation is conserved and will be determined by formula (42).

The development of methods of optical orientation in semiconductors reveals a large number of possibilities

for investigating by elementary means the kinetics of recombination and the spin relaxation of electrons, the special features of the band structure determined by the spin-orbit coupling, and also the characteristics of the interaction of oriented electrons with paramagnetic centers.

<sup>1</sup>C. Cohen-Tannoudji and A. Kastler, in *Progress in Optics*, edited by E. Wolf (North-Holland Publishing Co., Amsterdam, The Netherlands, 1966), Vol. 5, p. 33.

<sup>2</sup>Georges Lampel, *Phys. Rev. Letters* **20**, 491 (1968).

<sup>3</sup>R. R. Parsons, *Phys. Rev. Letters* **23**, 1152 (1969); *Proceedings of the Tenth International Conference on the Physics of Semiconductors*, Cambridge, Massachusetts, 1970, p. 814.

<sup>4</sup>A. I. Ekimov and V. I. Safarov, *ZhETF Pis. Red.* **12**, 293 (1970) [*JETP Lett.* **12**, 198 (1970)]; D. Z. Garbuzov,

A. I. Ekimov, and V. I. Safarov, *ZhETF Pis. Red.* **13**, 36 (1971) [*JETP Lett.* **13**, 24 (1971)].

<sup>5</sup>B. P. Zakharchenya, V. G. Flejšer, R. I. Dzhioev, Yu. Veshchunov, and I. B. Rusanov, *ZhETF Pis. Red.* **13**, 195 (1971) [*JETP Lett.* **13**, 137 (1971)].

<sup>6</sup>M. I. D'yakonov and V. I. Perel', *ZhETF Pis. Red.* **13**, 206 (1971) [*JETP Lett.* **13**, 144 (1971)].

<sup>7</sup>Charles Kittel, *Quantum Theory of Solids*, Wiley, 1963 (Russ. Transl., Nauka, 1967).

<sup>8</sup>E. O. Kane, *J. Phys. Chem. Solids* **1**, 82 (1956).

<sup>9</sup>J. M. Luttinger, *Phys. Rev.* **102**, 1030 (1956).

<sup>10</sup>A. Edmonds, CERN 55-26, Geneva, 1955.

<sup>11</sup>N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.* **73**, 679 (1948).

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213