Optical orientation of excitons in uniaxial crystals. Large exchange splitting

G. L. Bir and G. E. Pikus
A. F. Ioffe Physico-technical Institute, USSR Academy of Sciences
(Submitted November 22, 1972)
Zh. Eksp. Teor. Fiz. **64**, 2210-2221 (June 1973)

The degree of polarization of luminescence from excitons and its variation induced by a magnetic field or by deformation are calculated for various methods of exciton excitation in crystals with a wurtzite structure. It is demonstrated that when the excitons are oriented, new effects should be observed which are absent when the free carriers are oriented. Thus, linearly polarized radiation arises on excitation by linearly polarized light; in a transverse magnetic field and following lateral deformation, circularly polarized luminescence may arise upon excitation by linearly polarized light, or linearly polarized light may arise upon excitation by circularly polarized light. It is shown that measurement of the degree of orientation in an inclined magnetic field permits one to separate exciton effects from effects which are produced by free carriers and which may be superimposed upon formation of excitons by electron-hole binding.

INTRODUCTION

The use of optical orientation and, in particular, the study of polarized luminescence, uncovers new possibilities for the study of excitation spectra in crystals and of their interaction, as is evidenced, e.g., by a number of studies[1] of optical orientation of free carriers.

In this paper we consider optical orientation of excitons, and in particular the influence exerted on it by an external magnetic field and by deformation. We show that optical orientation of excitons has a number of features that distinguish it from the optical orientation of free carriers. Thus, excitons can be not only oriented, like free carriers, upon excitation by circularly-polarized light, but can also become aligned when excited with linearly polarized light. Under external influences, one type of orientation can go over into another, just as in the case of optical excitation of atoms in gases[2]. The features of these effects depend essentially on the character of the exciton spectrum, and in particular on its fine structure, which is determined by the symmetry of the crystal and by the type of the band structure.

In this paper we consider optical orientation of excitons in uniaxial crystals with wurtzite structure, the exciton spectra of which have been thoroughly investigated and in which optical orientation of excitons has been observed[3]. The formulas derived are applicable also for most other uniaxial crystals, in particular for crystals of the GaSe type, in which polarized exciton luminescence was also observed[4]. (Orientation of excitons in cubic crystals has recently been reported in[5]).

In the first part of the paper we consider the case of large exchange splitting; the case of small splitting will be considered in the second part. The change of the optical orientation under the influence of external actions is essentially different in these two cases[1)]

1. EXCITONS IN CRYSTALS WITH WURTZITE STRUCTURE

1. Wave functions and spectrum. In A_2B_6 and A_3B_5 crystals with wurtzite structure there are three closely-located valence bands Γ_9, Γ_7, Γ_7, stemming from the p band as a result of crystal and spin-orbit splittings Δ_{cr} and Δ_{so}, and the conduction band corresponds to the representation Γ_7. In these crystals, three series of excitons are observed: $A(\Gamma_7 \times \Gamma_9)$, B, and $C(\Gamma_7 \times \Gamma_7)$. The ground state of each of these excitons is quadruply degenerate and splits, in accord with the group-theoretical rules, into two states for the exciton A and three states for the excitons B and C:

$$\Gamma_7 \times \Gamma_9 = \Gamma_5 + \Gamma_6, \quad \Gamma_7 \times \Gamma_7 = \Gamma_1 + \Gamma_2 + \Gamma_5 \tag{1}$$

This splitting is described by the spin (exchange) Hamiltonian

$$\begin{aligned} &\mathcal{H} = \Delta_\parallel(\sigma_z^e\sigma_z^h) + 2\Delta_\perp(\sigma_+^e\sigma_-^h + \sigma_-^e\sigma_+^h) && (\Gamma_7 \times \Gamma_7 \text{ exciton}),\\ &\mathcal{H} = \bar{\Delta}_\parallel(\sigma_z^e\sigma_z^h) && (\Gamma_7 \times \Gamma_7 \text{ exciton}), \end{aligned} \tag{2}$$

where $\sigma_\pm = 1/2(\sigma_x \pm i\sigma_y)$. Here σ^e and σ^h are Pauli matrices in the basis of the electronic and hole functions $\psi_{\pm 1/2}$ and $\varphi_{\pm 1/2}$ for the exciton $\Gamma_7 \times \Gamma_7$ and in the basis of hole functions $\varphi_{\pm 3/2}$ for the exciton $\Gamma_7 \times \Gamma_9$.[2)]

Each exciton wave function is a product of a smooth function by a combination of products of band functions of the electrons ψ and of the holes φ, which determine the exciton spin. For exciton functions that transform in accordance with the irreducible representations (1), we choose the indicated spin functions in the form

$$\begin{aligned} &\Phi_1 = \psi_{1/2}\varphi_{1/2}, \quad \Phi_2 = \psi_{-1/2}\varphi_{-1/2}, \quad E_{1,2} = \Delta_\parallel \quad (\Gamma_5),\\ &\Phi_{3,4} = (\psi_{1/2}\varphi_{-1/2} \pm \psi_{-1/2}\varphi_{1/2})/\sqrt{2}, \quad E_{3,4} = -\Delta_\parallel \pm 2\Delta_\perp \quad (\Gamma_{1,2}), \end{aligned} \tag{3a}$$

for the $\Gamma_7 \times \Gamma_7$ exciton and

$$\begin{aligned} &\Phi = \psi_{-1/2}\varphi_{3/2}, \quad \Phi_2 = \psi_{1/2}\varphi_{-3/2}, \quad E_{1,2} = -\Delta_\parallel \quad (\Gamma_5),\\ &\Phi_3 = \psi_{1/2}\varphi_{3/2}, \quad \Phi_4 = \psi_{-1/2}\varphi_{-3/2}, \quad E_{3,4} = \Delta_\parallel \quad (\Gamma_6) \end{aligned} \tag{3b}$$

for the $\Gamma_7 \times \Gamma_9$ exciton. In the case considered by us, when both the incident and the emitted light propagate along the principal axis z, the only optically active states are Γ_5, corresponding to the functions $\Phi_{1,2}$.

2. Luminescence polarization. The tensor $d_{\alpha\beta}$; which determines the exciton luminescence polarization, is connected with the components of the exciton density matrix ρ by the relation

$$d_{\alpha\beta} = \sum_{ij} \rho_{ij} j_i^\alpha j_j^{\beta *}. \tag{4}$$

Here j_i are the matrix elements of the current operator, which determine the probability of the excitation of the

exciton in the state i. For the excitons $\Gamma_7 \times \Gamma_7$ and $\Gamma_7 \times \Gamma_9$, the nonzero matrix elements are $j_1^- = j_2^+$, and for the exciton $\Gamma_7 \times \Gamma_7$ the element j_3^z also differs from zero. (Here $j^\pm = (j^x \pm ij^y)/\sqrt{2}$). The matrix $d_{\alpha\beta}$ determines the mean value of the product $\mathscr{E}_\alpha \mathscr{E}_\beta^*$, where $\mathscr{E}$ is the field intensity of the light wave. Here $d_{\alpha\alpha} = |\mathscr{E}_\alpha|^2$, $d_{xy} = \mathscr{E}_x \mathscr{E}_y^*$, and $d_{+-} = \mathscr{E}_+ \mathscr{E}_-^*$, where $\mathscr{E}_\pm = (\mathscr{E}_x \pm i\mathscr{E}_y)/\sqrt{2}$. In accordance with the selection rules indicated above for light propagating along the z axis, the degree of circular polarization of exciton luminescence, both for the $\Gamma_7 \times \Gamma_7$ exciton and for the $\Gamma_7 \times \Gamma_9$ exciton, is

$$\mathscr{P}_{\text{circ}} = \frac{d_{++} - d_{--}}{d_{++} + d_{--}} = \frac{\rho_{11} - \rho_{22}}{\rho_{11} + \rho_{22}}, \tag{5}$$

and the degree of linear polarization is equal to

$$\mathscr{P}_{\text{exc}} = \frac{2|d_{+-}|}{d_{++} + d_{--}} = \frac{2|\rho_{12}|}{\rho_{11} + \rho_{22}} \tag{6}$$

The polarization-plane direction characterized by the angle φ (reckoned from the x axis) is determined by the phase $\rho_{12} = |\rho_{12}|e^{i\psi}$, and recognizing that $d_{+-} = |d_{+-}|e^{2i\varphi}$, we obtain from (4)

$$\varphi = -\tfrac{1}{2}\psi. \tag{7}$$

2. DENSITY MATRIX FOR EXCITONS

To determine the degree of the radiation polarization it is necessary to determine the exciton density matrix. In the stationary case the components ρ_{ij} satisfy the equation

$$-\left(\frac{\partial \rho_{ij}}{\partial t}\right)_{\text{rec}} - \left(\frac{\partial \rho_{ij}}{\partial t}\right)_{\text{rel}} + \frac{i}{\hbar}[\mathscr{H}\rho]_{ij} + \frac{i}{\hbar}(E_i - E_j)\rho_{ij} = G_{ij}. \tag{8}$$

The first two terms determine here the change of the density matrix as a result of recombination (and decay) and of spin-relaxation processes. The third term determines the change of the density matrix due to the external fields. The matrix components G_{ij} determine the rate of generation of the density-matrix components ρ_{ij}.

1. Generation rate. The rate of generation of the components ρ_{ij} depends essentially on the method of exciton generation. We consider here two principal methods of generation—resonant excitation and exciton production by pair binding.

A. In the case of resonant excitation of the excitons, the generation rate G_{ij} is determined by the polarization tensor $d^0_{\alpha\beta}$ of the incident light and depends on the selection rules:

$$G_{ij} \sim \sum_{\alpha\beta} d_{\alpha\beta}{}^0 j_i^{\alpha *} j_j^\beta. \tag{9}$$

Consequently, in resonant excitation of $\Gamma_7 \times \Gamma_7$ and $\Gamma_7 \times \Gamma_9$ excitons we have

$$G_{11} \sim d_{++}{}^0 = |\overline{\mathscr{E}_+}|^2, \quad G_{22} \sim d_{--}{}^0 = |\overline{\mathscr{E}_-}|^2, \quad G_{12} \sim d_{-+}{}^0 = \overline{\mathscr{E}_-\mathscr{E}_+^*}. \tag{9a}$$

In the case of excitation with circularly-polarized light, the component ρ_{11} or ρ_{22} is excited, and in case of excitation with linearly polarized light we have

$$G_{11} = G_{22} = \tfrac{1}{2}G_0, \; G_{12} = \tfrac{1}{2}G_0 e^{-2i\varphi_{\mathscr{E}}}, \tag{9b}$$

where $\varphi_{\mathscr{E}}$ is the azimuthal angle and determines the position of the polarization plane of the incident light.

B. When excitons are produced by binding of electron and hole pairs, the matrix G is determined by the state of the free carriers. The density matrix for the free electrons and holes is a product of the electron and hole matrices, $\rho_{eh} = \rho_e \rho_h$.

If the exchange splitting is small in comparison with the exciton binding energy, then no noticeable electron and hole spin correlation should take place in the binding process, and in this case the matrix G in the corresponding basis is also a direct product of two matrices, G_e and G_h, which determine the state of the electron or hole immediately after their binding into an exciton:

$$G = G_e G_h. \tag{10}$$

If the components of the matrices G_e and G_h in the bases ψ_n and φ_m of the electron and hole functions are respectively equal to $G^e_{nn'}$ and $G^h_{mm'}$, and the spin wave function of the exciton is

$$\Phi_i = \sum_{mn} C_{i,nm} \psi_n \varphi_m, \tag{11}$$

then, according to (10), in the basis of the function Φ_i, we have

$$G_{ij} = \sum_{mnm'n'} C^*_{i,nm} C_{j,n'm'} G^e_{nn'} G^h_{mm'}. \tag{12}$$

When electron-hole pairs are excited by light, only diagonal components of the density matrices ρ_e and ρ_h are generated (in the basis of the functions $\psi^e_{1,2} = \psi_{\pm 1/2}$, $\psi^h_{1,2} = \varphi_{\pm 1/2}$ (Γ_7), $\varphi^h_{1,2} = \varphi_{\pm 3/2}$ (Γ_9)). Then

$$\rho^{e,h}_{11} = \tfrac{1}{2}n_0(1 + p_{e,h}), \quad \rho^{e,h}_{22} = \tfrac{1}{2}n_0(1 - p_{e,h}), \tag{13}$$

where $p_{e,h}$ is the degree of orientation of the electrons or holes, and n_0 is their number. It is obvious that in this case only diagonal components of the matrices G_e and G_h can be generated, and the ratios

$$(G^{e,h}_{11} - G^{e,h}_{22})/(G^{e,h}_{11} + G^{e,h}_{22}) = p'_{e,h} \tag{14}$$

are proportional to the degree of orientation of the free carriers $p_{e,h}$, i.e., $p'_{e,h} = \alpha_{e,h} p_{e,h}$. If the spin of the electrons and holes does not change during the process of pair binding, then $p'_{e,h} = p_{e,h}$, but if this process is accompanied by a partial relaxation of the spins, then $\alpha_{e,h} < 1$.

It follows from (12) and (14) that the components of the matrix G_{ij} in the basis (3a) or (3b) are expressed in the following manner in terms of the coefficients p'_e and p'_h. For the $\Gamma_7 \times \Gamma_7$ exciton:

$$\begin{gathered} G_{11} = \tfrac{1}{4}N_0(1 + p_e')(1 + p_h'), \quad G_{22} = \tfrac{1}{4}N_0(1 - p_e')(1 - p_h'), \\ G_{33} = G_{44} = \tfrac{1}{4}N_0(1 - p_e'p_h'), \quad G_{34} = \tfrac{1}{4}N_0(p_e' - p_h'); \end{gathered} \tag{15}$$

and for the $\Gamma_7 \times \Gamma_9$ exciton:

$$\begin{gathered} G_{11} = \tfrac{1}{4}N_0(1 - p_e')(1 + p_h'), \quad G_{22} = \tfrac{1}{4}N_0(1 + p_e')(1 - p_h'), \\ G_{33} = \tfrac{1}{4}N_0(1 + p_e')(1 + p_h'), \quad G_{44} = \tfrac{1}{4}N_0(1 - p_e')(1 - p_h'), \end{gathered} \tag{16}$$

where N_0 is the total number of excitons produced per unit time. The remaining G_{ij} components are equal to zero.

2. Recombination rate and spin relaxation. The first term in (8), which describes the change of the density matrix as a result of departure, i.e., recombination and decay, is given in the general case by

$$\left(\frac{\partial \rho_{ij}}{\partial t}\right)_{\text{rec}} = -\frac{1}{2}\sum_m W_{im}\rho_{mj} + W_{mj}\rho_{im}. \tag{17}$$

The components of the matrix $W_{im} = W^*_{mi}$ can relate

only the components ρ_{ij} which transform under symmetry transformations. It is easily seen that for both the $\Gamma_7 \times \Gamma_7$ and $\Gamma_7 \times \Gamma_9$ exciton the matrix W is diagonal: $W_{ij} = W_{ii}\delta_{ij} = \tau_{ii}^{-1}\delta_{ij}$ and consequently

$$(\partial\rho_{ij}/\partial t)_{rec} = -\rho_{ij}/\tau_{ij}, \quad 2/\tau_{ij} = \tau_{ii}^{-1} + \tau_{jj}^{-1}. \tag{18}$$

For the $\Gamma_7 \times \Gamma_7$ and $\Gamma_7 \times \Gamma_9$ excitons we have $\tau_{11} = \tau_{22} = \tau_{12}$, and for the $\Gamma_7 \times \Gamma_9$ exciton also $\tau_{33} = \tau_{44} = \tau_{34}$.

The change of the component of the density matrix ρ_{ij} as a result of the spin relaxation is determined both by the departure terms, which are similar to (17), and by the arrival at the component ρ_{ij} from all other components, and in the general case the arrival term is given by

$$\left(\frac{\partial\rho_{ij}}{\partial t}\right)_{arr} = \sum_{mn} \mathscr{W}_{ijmn}\rho_{mn}. \tag{19}$$

where $\mathscr{W}_{ijmn} = \mathscr{W}^*_{jinm}$, and at $E_i = E_j$ and $E_m = E_n$ we have

$$\mathscr{W}_{mnij} = \mathscr{W}^*_{ijmn}\exp\{(E_m - E_i)/kT\}.$$

Just as in (17), the components $\mathscr{W}_{ijmn}$ can connect only those density-matrix components ρ_{ij} and ρ_{mn} which transform in like manner, i.e., only combinations of those components which transform like one and the same function of one and the same irreducible representation can be connected. For the term Γ_5 of the $\Gamma_7 \times \Gamma_7$ exciton, only arrival to $\rho_{11} + \rho_{22}$ from ρ_{33} and ρ_{44} is possible, and the relaxation of the components $\rho_{11} - \rho_{22}$ and ρ_{12} is determined only by the departure terms:

$$\begin{aligned}(\partial(\rho_{11} - \rho_{22})/\partial t)_{rel} &= -(\rho_{11} - \rho_{22})/\tau_{s1},\\ (\partial\rho_{12}/\partial t)_{rel} &= -\rho_{12}/\tau_{s2},\end{aligned} \tag{20}$$

Here $\tau_{s1} \neq \tau_{s2}$. (Arrival at $\rho_{11} - \rho_{22}$ from ρ_{34} and ρ_{43} is also possible for the $\Gamma_7 \times \Gamma_7$ exciton, but at $|E_3 - E_4| = 4|\Delta_\perp| \gg \hbar/\tau$ the components $\rho_{34} = \rho^*_{43}$ are practically equal to zero). For the $\Gamma_7 \times \Gamma_9$ exciton, it is possible to have, besides the arrival at $\rho_{11} + \rho_{22}$ from $\rho_{33} + \rho_{34}$, also arrival at $\rho_{11} - \rho_{22}$ from $\rho_{33} - \rho_{34}$ and at ρ_{12} from ρ_{43}.

3. OPTICAL ORIENTATION OF EXCITONS AND ITS VARIATION IN A MAGNETIC FIELD

1. Luminescence polarization in the absence of external fields. As follows from Eqs. (5), (6), (8), (18), and (20), under conditions when one can neglect the arrival (19) connected with the spin relaxation, the polarization of the exciton luminescence for the excitons $\Gamma_7 \times \Gamma_7$ and $\Gamma_7 \times \Gamma_9$ is determined by the expressions

$$\mathscr{P}^0_{circ} = \frac{G_{11} - G_{22}}{G_{11} + G_{22}}\frac{\tau_1}{\tau}, \quad \mathscr{P}^0_{lin} = \frac{2|G_{12}|}{G_{11} + G_{22}}\frac{\tau_2}{\tau}, \tag{21}$$

where $\tau = \tau_{11}$, $\tau_1^{-1} = \tau^{-1} + \tau_{s1}$, $\tau_2^{-1} = \tau^{-1} + \tau_{s2}^{-1}$.

In the case of resonant excitation by circularly- or linearly-polarized light, at $\tau_{s1}^{-1}, \tau_{s2}^{-2} \ll \tau^{-1}$, we have $\mathscr{P}^0_{circ} = 1$ or $\mathscr{P}^0_{lin} = 1$. When excitons are produced by binding of pairs, no linear polarization of the luminescence is produced, and the degree of the circular polarization of the luminescence is equal to

$$\mathscr{P}^0_{circ} = \frac{p_e' + p_h'}{1 + p_e' p_h'}\frac{\tau_1}{\tau} \quad (\Gamma_7 \times \Gamma_7),$$

$$\mathscr{P}^0_{circ} = \frac{p_h' - p_e'}{1 - p_h' p_e'}\frac{\tau_1}{\tau} \quad (\Gamma_7 \times \Gamma_9). \tag{22}$$

The last formulas differ from the expressions that determine the polarization of band-band luminescence only in that $p_{e,h}$ is replaced by $p^*_{e,h}$ and in the presence of the factor τ_1/τ.

2. Change of polarization in a magnetic field. The Hamiltonian $\mathscr{H}_H$ describing the influence of the magnetic field for the excitons $\Gamma_7 \times \Gamma_7$ and $\Gamma_7 \times \Gamma_9$ is given by

$$\mathscr{H}_H^{exc} = \mathscr{H}_H^e + \mathscr{H}_H^h, \tag{23}$$

where for electrons and holes we have

$$\mathscr{H}_H^{e,h} = {}^1/_2\mu[g_\parallel^{e,h}\sigma_z^{e,h}H_z + g_\perp^{e,h}(\sigma_+^{e,h}H_- + \sigma_-^{e,h}H_+)]. \tag{24}$$

Here μ is the Bohr magneton. $H_\pm = H_x \pm iH_y$.

For the Γ_9 holes we have in (24) $g_\perp^h = 0$. We note that in the case when the exciton binding energy is comparable with the distances between the valence bands, the constants $g_\perp^h$ and $g_\parallel^h$ in (23) and (24) can differ from the corresponding g-factors of the free holes.

A. The $\Gamma_7 \times \Gamma_7$ exciton. We consider the case of large exchange splitting, when $g\mu H \ll \Delta_\parallel, \Delta_\perp$. In this case we can consider separately the optically active state Γ_5.

For the state Γ_5 of the $\Gamma_7 \times \Gamma_7$ exciton in a weak transverse magnetic field, the Zeeman effect is quadratic in $H_\perp$, so that this field, as seen from (23), does not split the state Γ_5 directly. In second order of perturbation theory, the matrix element $\mathscr{H}^H_{12}$ is different from zero and is equal to

$$\mathscr{H}_{12}^H = \gamma H_-^2, \quad \gamma = \frac{1}{16}\mu^2\left/\left(\frac{(g_\perp^e + g_\perp^h)^2}{\Delta_\parallel - \Delta_\perp} - \frac{(g_\perp^e - g_\perp^h)^2}{\Delta_\parallel + \Delta_\perp}\right)\right. . \tag{25}$$

Accordingly, the splitting in the transverse field is $\Delta E_\perp = 2\gamma H_\perp^2$, and the splitting in the longitudinal field is linear in H_z:

$$\Delta E_\parallel = \mathscr{H}_{11}^H - \mathscr{H}_{22}^H = \mu(g_\parallel^e + g_\parallel^h)H_z. \tag{26}$$

Solving Eqs. (8) with (18), (20), (23), (25), and (26) taken into account, we obtain

$$\mathscr{P}_{circ}(H) = \frac{1}{1 + K^2}\{\mathscr{P}^0_{circ} - \mathscr{P}_{lin}(\tau_1/\tau_2)^{1/2}K\sin 2(\chi - \varphi')\}, \tag{27}$$

$$2\rho_{12}/(\rho_{11} + \rho_{22}) = e^{-2i(\varphi_E + \varphi')}\{\mathscr{P}^0_{lin}\cos 2\varphi' - iK(\tau_2/\tau_1)^{1/2}e^{-2i\chi}\mathscr{P}_{circ}(H)\}. \tag{28}$$

In the last formula, $\mathscr{P}_{circ}(H)$ is determined by expression (27), while $\mathscr{P}^0_{circ}$ and $\mathscr{P}^0_{lin}$ in these formulas are determined by (21) or (22),

$$K = \hbar^{-1}(\tau_1\tau_2)^{1/2}\Delta E_\perp/[1 + (\hbar^{-1}\tau_2\Delta E_\parallel)^2], \tag{29}$$

$$\chi = \varphi_H - \varphi_E, \quad \operatorname{tg} 2\varphi' = \hbar^{-1}\tau_2\Delta E_\parallel \quad (-\pi/4 < \varphi' \leqslant \pi/4), \tag{30}$$

φ_H is the azimuthal angle of the magnetic field. (Here $\Delta E_\perp$ and $\Delta E_\parallel$ can be of arbitrary sign, depending on the signs of γ and $g_\parallel^{e,h}$). The quantity φ_E determines the phase of $G_{12} = |G_{12}|\exp(-2i\varphi_E)$ and coincides at resonant excitation with the phase d^0_{+-} (expressions (9a) and (9b)).

In accord with (6) and (28), the degree of linear polarization of the luminescence is given by the formula

$$\mathscr{P}_{lin}(H) = \left\{\mathscr{P}^{02}_{lin}\cos^2 2\varphi' + \mathscr{P}^2_{circ}(H)K^2\frac{\tau_2}{\tau_1} + 2\mathscr{P}^0_{lin}\mathscr{P}_{circ}(H)K\left(\frac{\tau_2}{\tau_1}\right)^{1/2}\cos 2\varphi'\sin 2\chi\right\}^{1/2}. \tag{31}$$

It follows from (27)—(31) that in the case of resonant excitation by circularly polarized light, or when ex-

citons are produced by pair binding, we have

$$\mathscr{P}_{\text{circ}}(H)=\frac{\mathscr{P}^0_{\text{circ}}}{1+K^2},\quad \mathscr{P}_{\text{lin}}(H)=\frac{|\mathscr{P}^0_{\text{circ}}K|}{1+K^2}\left(\frac{\tau_2}{\tau_1}\right)^{1/2}. \tag{32}$$

The angle between the plane of polarization and the magnetic field is in this case

$$\varphi-\varphi_H=\varphi'-\frac{\pi}{4}\operatorname{sign}\gamma\mathscr{P}_{\text{circ}}. \tag{33}$$

B. In a transverse magnetic field when $K=\hbar^{-1}(\tau_1\tau_2)^{-1/2}\Delta E_\perp$, $\mathscr{P}_{\text{circ}}(H)$ decreases to zero with increasing $H_\perp$, and $\mathscr{P}_{\text{lin}}(H)$ reaches a maximum at K = 1, after which it also decreases. The depolarization curve $\mathscr{P}_{\text{circ}}(H)$ has in this case not a Lorentz shape, as in the usual Hanle effect, but is proportional to $(1+\alpha H_\perp^4)^{-1}$, and therefore the decrease of $\mathscr{P}_{\text{circ}}(H)$ is more rapid and begins in stronger fields: the field corresponding to K = 1 is larger by a factor $(\hbar^{-1}\tau_{1,2}\Delta)^{1/2}$ than the ordinary Hanle fields $H\sim\hbar/g\mu\tau$. In the case of resonant excitation of excitons by linearly polarized light in a transverse magnetic field, when $\varphi'=0$, we have

$$\mathscr{P}_{\text{circ}}(H)=-\mathscr{P}^0_{\text{lin}}\frac{K}{1+K^2}\left(\frac{\tau_1}{\tau_2}\right)^{1/2}\sin 2\chi, \tag{34}$$

$$\mathscr{P}_{\text{lin}}(H)=\mathscr{P}^0_{\text{lin}}\left[\cos^2 2\chi+\frac{\sin^2 2\chi}{(1+K^2)^2}\right]^{1/2}.$$

We see that in this case the effects have a characteristic angular dependence: at $\chi\neq 0$ or $\pi/2$ the degree of linear polarization in a transverse magnetic field decreases, and circular polarization appears. The plane of polarization is then rotated through an angle $\Delta\varphi$:

$$\Delta\varphi=\frac{1}{2}\operatorname{arctg}\frac{K^2\sin 4\chi}{2(1+K^2\cos^2 2\chi)},\quad -\frac{\pi}{4}<\varphi\leqslant\frac{\pi}{4}. \tag{35}$$

Since the transverse magnetic field exerts an appreciable influence on the polarization at $K\sim 1$, i.e., at $\gamma H_\perp^2\sim\hbar/\tau$, and the formulas of this sections are applicable at $g_\perp\mu H_\perp\ll\Delta_\parallel$, $\Delta_\perp$, the condition for the applicability of the approximation of large exchange splitting is $\Delta_\parallel$, $\Delta_\perp\gg h/\tau_{1,2}$.

C. In a longitudinal magnetic field K = 0 and the degree of circular polarization of the radiation does not change, while linear polarization is produced only by excitation with linearly polarized light and decreases in the magnetic field in accordance with the law

$$\mathscr{P}_{\text{lin}}=\mathscr{P}^0_{\text{lin}}\cos 2\varphi'=\mathscr{P}^0_{\text{lin}}/[1+(\hbar^{-1}\tau_2\Delta E_\parallel)^2]^{1/2}. \tag{36}$$

The polarization plane rotates in this case through an angle φ'.

If the field is oblique and makes an angle ϑ with the z axis, then the ratio

$$\frac{\Delta E_\perp}{\Delta E_\parallel}\sim\frac{\gamma H_\perp^2}{g\mu H_z}\sim\frac{g\mu H}{\Delta}\frac{H_\perp}{H_z}$$

is small, since $g\mu H\ll\Delta$, provided only that the angle ϑ is not close to $\pi/2$, and consequently under these conditions $K\approx 0$ and the longitudinal component of the field predominates. The transverse component $H_\perp$ can come into play only if

$$\pi/2-\vartheta\leqslant(\hbar/\Delta_{\perp,\parallel}\tau_{1,2})^{1/2}.$$

D. The $\Gamma_7\times\Gamma_9$ exciton. For the $\Gamma_7\times\Gamma_9$ exciton, for which $\gamma=0$ and $g_\perp^h=0$, we also have $\gamma=0$, as seen from (25). For this exciton, there is no Zeeman effect in a transverse field at all. Therefore a transverse magnetic field does not influence its orientation so long as $g_\perp^e\mu H_\perp<\Delta_\parallel$, i.e., so long as there is no intermixing of the terms Γ_5 and Γ_6, and the polarization of the electron luminescence does not change in fields $H_\perp\ll\Delta_\parallel/\mu g_\perp^e$. The change of the linear polarization in a longitudinal field is determined by formula (36), just as for the $\Gamma_7\times\Gamma_7$ exciton.

3. Change of generation rate in a magnetic field. In the formulas presented above it is assumed that the magnetic field does not affect directly the generation rate G_{ij}. In the case of resonant excitation this assumption holds true. But if the excitons are produced by pair binding, if the carrier lifetime prior to the binding is not very short, the magnetic field can noticeably alter their orientation, and this leads in accord with (15) to a change of G_{ij}. The change of the orientation of the electrons and holes in a magnetic field is determined by an equation similar to (8), and it follows from (24) that

$$p_{e,h}(H)=p^0_{e,h}/(1+L^2_{e,h}), \tag{37}$$

where

$$L^2=L_\perp^2/(1+L_\parallel^2),\quad L_\perp=\mu g_\perp^{e,h}H_\perp(\tau_1^{e,h}\tau_2^{e,h})^{1/2}\hbar^{-1}$$

$$L_\parallel=\mu g_\parallel^{e,h}H_z\tau_2^{e,h}\hbar^{-1}.$$

Here $\tau_1^{e,h}$ and $\tau_2^{e,h}$ are the relaxation times of the components $\rho_{11}^{e,h}-\rho_{22}^{e,h}$ and $\rho_{12}^{e,h}$, respectively, which are determined both by the binding time and by the other recombination mechanisms, as well as by the spin relaxation.

In a transverse field the values of $p_{e,h}(H_\perp)$ for electrons and holes of Γ_7 decrease to zero with increasing $H_\perp$, owing to the Hanle effect, and in an oblique field $p_{e,h}$ remains finite as $H\to\infty$:

$$p^{e,h}(\infty)=p^0_{e,h}\frac{\tau_1^{e,h}}{\tau_2^{e,h}}\Big/\left[1+\frac{g_\parallel^2}{g_\perp^2}\operatorname{ctg}^2\theta\right]. \tag{38}$$

In addition to changing the component $\rho_{11}^{e,h}-\rho_{22}^{e,h}$, the magnetic field gives rise to the appearance of the component $\rho_{12}^{e,h}$:

$$2\rho_{12}^{e,h}/(\rho_{11}^{e,h}+\rho_{22}^{e,h})=L_{e,h}p_{e,h}(H)e^{-i(\psi_{e,h}+\varphi_H)}. \tag{39}$$

Here φ_H is the angle that determines the appearance of the transverse component of the magnetic field, and

$$\psi_{e,h}=-\operatorname{arctg}L_z^{e,h}. \tag{40}$$

Here $-\pi/2<\psi\leq\pi/2$ at $g_\perp L_z>0$ and $\pi/2<\psi<3\pi/2$ at $g_\perp L_z<0$. Therefore in a transverse magnetic field there can be generated the components $G_{12}^{e,h}$ which lead to the appearance of an exciton component $G_{12}=G_{12}^eG_{12}^h$, and which also contribute to the components G_{33}, G_{44}, G_{13}, G_{14}, G_{23}, G_{24}, and G_{34} of the $\Gamma_7\times\Gamma_7$ exciton and the components G_{13}, G_{14}, G_{23}, and G_{24} of the $\Gamma_7\times\Gamma_9$ exciton, for which $G_{12}^h=0$. Therefore in the case when the excitons are produced by pair binding and their depolarization in the magnetic field is significant, it is necessary to replace $\mathscr{P}^0_{\text{circ}}$ in formulas (27), (28), (31), and (32) by $\mathscr{P}^0_{\text{circ}}(H)$:

$$\mathscr{P}^0_{\text{circ}}(H)=\frac{p_e'(H)+p_h'(H)}{1+p_e'(H)p_h'(H)}\quad(\Gamma_7\times\Gamma_7),$$

$$\mathscr{P}^0_{\text{circ}}(H)=\frac{p_h'-p_e'(H)}{1-p_h'p_e'(H)}\quad(\Gamma_7\times\Gamma_9). \tag{41}$$

The $p'_{e,h}(H)$ dependence is determined here by a formula similar to (37).

Owing to the generation of G_{12}, an initial linear polarization is also produced. To take it into account it is

necessary to replace in (27), (28), and (31) $\mathcal{P}^0_{\text{lin}}$ by $\mathcal{P}^0_{\text{lin}}(H)$, which, according to (8), (21), and (39) is determined by the formula

$$\mathcal{P}^0_{\text{lin}}(H)=\frac{|p_e^0 p_h^0 L_e L_h|}{(1+L_e^2)(1+L_h^2)+p_e^0 p_h^0}\frac{\tau}{\tau_2}\left(\frac{\tau_2^e\tau_2^h}{\tau_1^e\tau_1^h}\right)^{1/2}. \quad (42)$$

We see that a noticeable degree of linear polarization $\mathcal{P}^0_{\text{lin}}(H)$ can be observed only in an intrinsic semiconductor, if both types of carrier are oriented and the times $\tau^e_{1,2}$ and $\tau^h_{1,2}$ are close to each other. The maximal degree of polarization is reached at $L_e \approx L_h \approx 1$ and does not exceed $0.25p_e^0p_h^0$. In accordance with (7), (16), (40), and (41), the angle φ between the plane of polarization and the transverse component of the magnetic field is equal to $\chi = \varphi_H - \varphi_{\mathcal{E}} = -1/2(\psi_e + \psi_h)^{3)}$.

From formulas (27)--(29) and (37) and (39) it follows that under different conditions there can predominate either the exciton or the electron effects: in a transverse field the orientation of the electrons (or holes), and consequently also the magnitude of $\mathcal{P}^0_{\text{circ}}(H)$ are significantly altered when $g\mu H \sim \hbar/\tau_{e,h}$, whereas the orientation of the excitons and accordingly $\mathcal{P}(H)$ in (27)–(29) change significantly at $\gamma H^2 \sim (g\mu H)^2/\Delta \sim \hbar/\tau_{1,2}$, i.e., at $g\mu H \sim (\hbar\Delta/\tau_{1,2})^{1/2}$. Therefore, if $\tau_{e,h} \gg (\hbar\tau_{1,2}/\Delta)^{1/2}$, the change of the degree of polarization is determined by the electronic effects, i.e., by the change of $\mathcal{P}^0_{\text{circ}}(H)$, and in this case no linear polarization of the radiation is usually produced, and $\mathcal{P}_{\text{circ}}(H)$ is of the Lorentz type.

On the other hand, if $\tau_{e,h} \ll (\hbar\tau_{1,2}/\Delta)^{1/2}$, then the change of $\mathcal{P}^0_{\text{circ}}(H)$ in (43) can, to the contrary, be neglected, since the magnetic field alters significantly the orientations until extinction of the electron orientation begins.

The exciton and electron effects can be distinguished both by the dependence of the degree of polarization on the transverse magnetic field, and by its change with changing field direction: at angles $1 \gg 1/2\pi - \vartheta \gg (\hbar/\tau_{1,2}\Delta)^{1/2}$ the excitonic Hanle effect vanishes, and the electronic effect remains practically unchanged. In this case the Hanle effect in the inclined field can be used to determine, in accord with (38) and (40), the ratio of the g-factors $g^{e,h}_{\parallel}/d^{e,h}_{\perp}$.

We note that if the character of the dependence of $\mathcal{P}(H)$ on the magnetic field remains the same when an appreciable role is assumed by the arrival terms (18), arrival can only change the initial polarizations $\mathcal{P}^0_{\text{lin}}$ and $\mathcal{P}^0_{\text{circ}}$. The character of the $\mathcal{P}(H)$ dependence can be altered by arrival only when the excitons are produced by pair binding, if both the electrons and the holes are oriented in this case.

4. CHANGE OF THE OPTICAL ORIENTATION OF THE EXCITONS UPON DEFORMATION

The deformation of the crystal leads both to a change in the value of the existing exchange splitting, and to an additional splitting of the degenerate states and to their mixing.

In wurtzite, for the $\Gamma_7 \times \Gamma_7$ and $\Gamma_7 \times \Gamma_9$ excitons, the deformations ϵ_{zz} and $\epsilon_\perp = \epsilon_{xx} + \epsilon_{yy}$ only change the constants $\Delta_\parallel$, $\Delta_\perp$, and $\overline{\Delta}_\parallel$, and the splitting or mixing of different states can occur at deformations $\epsilon_\pm = \epsilon_{xx} - \epsilon_{yy} \pm 2i\epsilon_{xy}$ and $\epsilon_{\pm z} = \epsilon_{xz} \pm i\epsilon_{yz}$. Therefore such deformations can influence the optical orientation of the excitons. The corresponding Hamiltonian $\mathcal{H}_\epsilon$ is given by[4)]

$$\begin{aligned}\mathcal{H}_\epsilon &= C_1(\sigma_+^e\sigma_+^h\varepsilon_- + \sigma_-^e\sigma_-^h\varepsilon_+) + C_2\sigma_z^e(\sigma_+^h\varepsilon_{-z} + \sigma_-^h\varepsilon_{+z}) \\ &\quad + C_3\sigma_z^h(\sigma_+^e\varepsilon_{-z} + \sigma_-^e\varepsilon_{+z}) \quad (\Gamma_7\times\Gamma_7),\\ \mathcal{H}_\epsilon &= (C_1\sigma_+^h + C_2\sigma_-^h)\sigma_-^e\varepsilon_- + (C_2\sigma_+^h + C_1\sigma_-^h)\sigma_+^e\varepsilon_+ \\ &\quad + C_3\sigma_z^h(\sigma_+^e\varepsilon_{-z} + \sigma_-^e\varepsilon_{+z}) \quad (\Gamma_7\times\Gamma_9).\end{aligned} \quad (43)$$

The change of the exchange splitting upon deformation is due to the change of the wave functions as a result of the mixing of the functions of the neighboring valence bands. Therefore the constants C_i in (43) are of the order of $D_i\Delta_{\text{exc}}/\delta E$, where δE is the distance between the nearest valence bands, and D_i is the band constant of the deformation potential, which determines the change δE under the corresponding deformation. Thus, in the quasicubic approximation, i.e., at $\Delta_{\text{cr}} \ll \Delta_{\text{so}}$, the constants C_i in (43) are equal in the isotropic case to

$$\begin{aligned}C_1 = C_2 = C_3 = \sqrt{3}d\Delta_1/\Delta_{\text{cr}} \quad (\Gamma_7\times\Gamma_9),\\ C_1 = C_3 = \sqrt{3}d\Delta_1/\Delta_{\text{cr}}, \quad C_2 = 0 \quad (\Gamma_7\times\Gamma_7).\end{aligned} \quad (44)$$

In the quasicubic approximation, the distance between the band Γ_9 and the nearest band Γ_7 is equal to Δ_{cr}, and the exchange constants for the excitons A and B are connected by the relation $2\Delta_\parallel = \Delta_\perp = -2\overline{\Delta}_\parallel = \Delta_1$. In (44), d is one of the shear constants of the deformation potential of the valence band, which is connected in the isotropic case with the other constant b by the relation $d = \sqrt{3}b$ (see[10], Secs. 30 and 40). According to the data of[11] and in accord with the indicated estimates, the values of the constants C_1 for CdS and ZnO are equal to approximately 1 eV.[5)]

It is seen from (40) that in the approximation linear in ϵ the splitting of the degenerate states Γ_5 and Γ_6 occurs only at deformations $\epsilon_\pm$, and the corresponding matrix elements are equal to

$$\mathcal{H}^\epsilon_{1,2} = C_1\varepsilon_-(\Gamma_5), \quad \mathcal{H}^\epsilon_{3,4} = C_2\varepsilon_+(\Gamma_6). \quad (45)$$

Therefore the deformation $\epsilon_\pm$ influences the optical orientation of the excitons in the same manner as the field $H_\perp$, and the change of the polarization of the exciton luminescence by the deformation $P(\epsilon)$ is described by formulas (27), (28), and (31–35). Then

$$K = h^{-1}(\tau_1\tau_2)^{1/2}\Delta E_\epsilon, \quad \varphi' = 0, \quad (46)$$

where $\Delta E_\epsilon = C_1[\epsilon_{xx} - \epsilon_{yy})^2 + 4\epsilon_{xy}^2]^{1/2} = C_1|\epsilon_1 - \epsilon_2|$. Here ϵ_1 and ϵ_2 are the principal values of the tensor ϵ in the xy plane. The angle φ_H must be replaced in the indicated formulas by φ_ϵ:

$$\varphi_\epsilon = {}^1/_2 \operatorname{arctg}[2\varepsilon_{xy}/(\varepsilon_{xx} - \varepsilon_{yy})].$$

Here $-\pi/4 < \varphi_\epsilon \leq \pi/4$ at $\epsilon_{xx} - \epsilon_{yy} > 0$ and $\pi/4 < \varphi_\epsilon \leq 3\pi/4$ at $\epsilon_{xx} - \epsilon_{yy} < 0$. Accordingly, χ is replaced by $\varphi_\epsilon - \varphi_{\mathcal{E}}$, and sign γ in (33) is replaced by sign C_1.

Unlike the magnetic field, the deformation does not change the generation rate. Therefore the indicated formulas describe completely the change of the polarization by deformation, regardless of the excitation method. They are equally applicable to the $\Gamma_7 \times \Gamma_7$ and to $\Gamma_7 \times \Gamma_9$ exction. The arrival terms in (18), just as in the case of the magnetic field, cannot change here the character of the $\mathcal{P}(\epsilon)$ dependence for the $\Gamma_7 \times \Gamma_7$ exciton. For the $\Gamma_7 \times \Gamma_9$ exciton, if the arrival terms play an essential role, the character of the $\mathcal{P}(\epsilon)$ dependence can change, since the deformation causes a splitting of the term Γ_6, which is connected by the arrival terms with the optically active term Γ_5; in this case the $\mathcal{P}(\epsilon)$ de-

pendence in resonant excitation, when only the state Γ_5 is excited, will be different from the case of exciton production by pair binding, when the excitons Γ_5 and Γ_6 are produced.

In conclusion, the authors thank M. I. D'yakonov and V. I. Perel' for valuable advice and discussions.

[1)]The result of the present paper are reported in part in brief communications [6,7].

[2)]For free excitons it is necessary in principle to take into account, besides the exchange interaction described by the Hamiltonian (2), also the annihilation interaction and the splitting connected with terms linear in K, which depend on the direction of the wave vector **K**. For bound excitons, the indicated mechanisms can make contributions to the constants $\Delta_{\|}$ and $\Delta_{\perp}$ [8,9]. The formulas presented below are therefore directly applicable to excitons bound with charged donors, acceptors, or neutron traps, and also to free excitons in which the annihilation splitting and the splitting linear in **K** are sufficiently small.

[3)]We note that a similar effect can arise, in principle, also in the case of direct band–band recombination, when the change of the polarization in the magnetic field is also determined by formulas (37), (39), and (42).

[4)]For holes of the Γ_9 band, the matrices σ_x^h and σ_y^h are transformed respectively in accordance with the representations Γ_3 and Γ_4, which enter in $\Gamma_7 \times \Gamma_9$, i.e., like $x_+^3 - x_-^3$ and $x_+^3 + x_-^3$. The remaining matrices σ_i are transformed like the corresponding components of the pseudovector J_i.

[5)]At sufficiently small Δ_{cr}, the indicated exchange-deformation effect can turn out to be for excitons an effective spin-relaxation mechanism.

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Translated by J. G. Adashko
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