Optical orientation and alignment of free excitons in GaSe during resonance excitation. Experiment

E. M. Gamarts, E. L. Ivchenko, M. I. Karaman, V. P. Mushinskiĭ, G. E. Pikus, B. S. Razbirin, and A. N. Starukhin

A. F. Ioffe Physicotechnical Institute, USSR Academy of Sciences, Leningrad
(Submitted April 6, 1977)
Zh. Eksp. Teor. Fiz. **73**, 1113–1127 (September 1977)

Polarized luminescence of excitons in GaSe crystals during resonance excitation in longitudinal and transverse magnetic fields has been investigated experimentally. When the excitons were subjected to resonance excitation by linearly or circularly polarized light, their emission was also found to be linearly or circularly polarized with high degree of polarization ($P = 0.93 \pm 0.05$), which indicated the presence of alignment and orientation of excitons, respectively. The longitudinal magnetic field ($\mathbf{H} \parallel c$, $\mathbf{H} \parallel \mathbf{k}_{light}$) gave rise to the depolarization of linearly polarized radiation from aligned excitons, but had practically no effect on the circular polarization of radiation emitted by oriented excitons. In the transverse magnetic field ($\mathbf{H} \perp c$, $\mathbf{H} \perp \mathbf{k}_{light}$), the depolarization effect depended on the angle between the plane of polarization of the exciting radiation and the direction of the magnetic field. In the case of resonance excitation of excitons by unpolarized light in a transverse magnetic field, the emitted radiation was linearly polarized with preferential polarization in the plane perpendicular to $\mathbf{H}_\perp$ because of the reduction in the intensity of radiation polarized in the plane containing $\mathbf{H}_\perp$. The transverse magnetic field was also found to give rise to depolarization of the circularly polarized exciton emission. The experimental data are in good agreement with microscopic theory,[8] and quantitative comparison with this theory yields the lifetime $\tau_0 = 1.6 \times 10^{-11}$ sec and exciton momentum relaxation time $\tau_p = 0.5 \times 10^{-11}$ sec for the specimens under investigation. A simple qualitative explanation of the observed effects is also given on the basis of the classical theory in which the free exciton is looked upon as a dipole oscillator rotating in a magnetic field.

PACS numbers: 78.20.Ls, 78.60.−b, 71.35.+z

INTRODUCTION

Optical orientation of excitons was originally achieved through optical orientation by circularly polarized light of free electrons and holes which were subsequently combined into excitons.[1,2] Direct excitation of exciton states by polarized light (under resonance conditions, and also during the generation of "hot" excitons) leads to a number of new effects characteristic only for the excitation of bound excitons.[3] The first to note is the alignment of excitons that is similar to the alignment of atoms in gases under excitation by linearly polarized light.[4–7] This effect does not occur for free carriers. Optical orientation results in the orientation of the magnetic moments of excitons, whereas alignment produces the orientation of their dipole moments in the absence of crystal magnetization. The Hanle effect (depolarization of exciton radiation in a magnetic field) plays an important role in the study of orientation and alignment, and provides important information both on the energy structure of exciton states and the relaxation of the excitations in time. Studies of the phenomenon of polarized[1)] exciton luminescence augment in an important way the traditional methods of investigating exciton states in crystals. There is considerable interest, in this connection, in the Hanle effect under resonance excitation. Razbirin *et al.*[6] have found some unusual features of the Hanle effect in GaSe crystals excited under such conditions, and have suggested that the observed anomalies were connected with the momentum relaxation of excited excitons.

The microscopic theory of optical orientation and alignment of free excitons under resonance excitation was developed in a previous paper[8] in which exciton emission was regarded as the result of resonance scattering of light during multiple elastic scattering of excitons excited by the light. In this paper, we report an experimental investigation of the polarized exciton luminescence in the case of GaSe crystals, considered theoretically in the previous paper.[8]

METHOD

The GaSe crystals were grown by Bridgman's method, without special doping, and the working specimens were produced by cleavage. The specimens can be divided into two types, depending on the shape of the edge luminescence spectra at low temperatures. The spectra of specimens of type I are dominated by emission lines due to free excitons, whereas impurity emission predominates in type II specimens. PF-42 film polarizers were used to produce and analyze linearly polarized radiation, and quarter-wave phase plates were used in the case of circularly polarized light. Such plates are usually made from a birefringent material of accurately specified thickness, and this is a very difficult operation. In addition to such plates, we therefore also used quarter-wave plates consisting of a combination of two parallel plates of mica of arbitrary thickness (within a very broad range of values), placed at a definite angle to each other. This is a very simple way of producing quarter-wave plates for any given wavelength.[9] The exciton luminescence was excited by radiation of spectral width ~0.01 eV and photon energy in the region of the absorption lines corresponding to the ground state of the $n = 1$ exciton.

The source of light was a spherical ultrahigh-pressure mercury lamp (DrSh-100-2). The required spectral band was defined either by a prism monochromator or by light filters. The exciting radiation was incident normally on the crystal surface, parallel to its optical c-axis, and

 0038-5646/77/4603-0590$02.40 © 1978 American Institute of Physics

the emission was recorded at a small angle to the direction of propagation of the exciting light. Superconducting solenoids were used to produce the magnetic fields. The investigations were carried out at $T = 2\ ^\circ K$.

EXPERIMENTAL RESULTS

The ground state of the $n = 1$ exciton in GaSe is quadruply degenerate. When the exchange interaction between the electron and the hole in the exciton is taken into account, this state is found to split.[8,10] The singlet state Γ_4 with resultant spin $S = 0$ splits off by the amount $\Delta_1 \approx 2$ meV. The triplet state with $S = 1$ splits into two terms in GaSe: Γ_6 with spin component along the optical c-axis $S_z = \pm 1$, and Γ_3 with $S_z = 0$. Data on the Zeeman effect in GaSe[10] show that the magnitude of this splitting is $\Delta \ll \Delta_1$. Transitions to Γ_4 are allowed when the light polarization is $\mathbf{E} \parallel c$, and transitions to Γ_6 are allowed for $\mathbf{E} \perp c$. The exciton Γ_3 is optically inactive.

The emission spectrum of type I GaSe in the region of the exciton transition under resonance excitation is shown in Fig. 1. As can be seen, the $n = 1$ line of the Γ_6 exciton has a doublet structure. According to Mooser and Schlüter,[10] this structure is due to the polytypic properties of GaSe crystals.[2)] We have investigated the component $\hbar\omega = 2.110$ eV (5874 Å) which was stronger in our specimens. The behavior of the weaker component was analogous in its main features.

1. Polarization in the absence of the magnetic field

Figure 1 shows the exciton emission spectra for two mutually perpendicular polarizations (along the X and Y axes) under excitation by linearly polarized light with $\mathbf{E} \parallel Y$. The direction of propagation was along the Z axis. Under resonance conditions, the linearly polarized light excites a state in the exciton with a given direction of the dipole moment ($\mathbf{P} \parallel \mathbf{E}$), which may be looked upon as a coherent superposition of the $S_z = 1$ and $S_z = -1$ states. Spin relaxation leads to a loss of correlation between the electron and hole dipole moments, produced when the exciton was created by linearly polarized light, and, consequently, to the disordering of the dipole moments of the excitons. If, however, the exciton lifetime τ_0 is less than, or comparable with, the time of its spin relaxation, then exciton emission will also be linearly polarized in the same plane as the exciting radiation. When this is so, we say that the excitons are aligned.

Let us define the degree of linear polarization by

$$\mathscr{P}_{\text{lin}} = \frac{I_Y - I_X}{I_Y + I_X}, \tag{1}$$

where I_Y and I_X are the intensities of radiation polarized in directions respectively parallel and perpendicular to the plane of polarization of the incident light. It is clear from Fig. 1 that the emission of a free exciton is highly polarized with $\mathscr{P}_{\text{lin}} = 0.93 \pm 0.05$.

We note that, when the crystal is excited by light with photon energy greater than the gap width ($\hbar\omega > E_g$), so that free-carrier generation takes place, the linear polarization of the radiation is not conserved. In fact, when excitons are produced by combining free carriers,

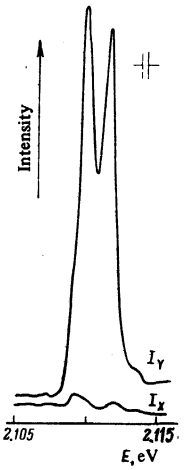

FIG. 1. Exciton emission spectra for $n = 1$ (Γ_6) from a GaSe crystal for two different polarizations: I_Y and I_X ($T = 2\ ^\circ K$).

a correlation between the dipole moments of electrons and holes is not found to appear because, under these conditions, the electrons and holes that combine to make the exciton are created in different photon-absorption events. This is the reason why excitation of a crystal by linearly polarized light with energy $\hbar\omega > E_g$ is not accompanied by alignment in the exciton system (provided only that hot excitons are not produced), and the linear polarization of the exciting radiation is not reflected in the emission of the system.

Only one of the exciton states, i.e., that with $S_z = 1$ or $S_z = -1$, is selectively populated in the case of circularly polarized exciting radiation because light with circular polarization σ^+ or σ^- corresponds to photons with angular momentum component ± 1 along the direction of propagation. This leads to the appearance in the crystal of a nonzero exciton magnetic moment, i.e., exciton orientation. This orientation is reflected in the fact that the emitted light is circularly polarized, with degree of polarization given by

$$\mathscr{P}_{\text{circ}} = \frac{I_+ - I_-}{I_+ + I_-}, \tag{2}$$

where I_+ and I_- are the intensities corresponding to right-handed and left-handed circular polarization. In the case of resonance excitation, the observed degree of polarization is very high: $\mathscr{P}_{\text{circ}} = 0.03 \pm 0.05$.

Because transitions are now possible between the three states corresponding to $S_z = 0, \pm 1$, the nature of the depolarization process due to spin relaxation of the exciton may be more complicated than in the case of orientation of free carriers. Moreover, the rates of relaxation of different components of the exciton density matrix are different. It follows that the degree of depolarization depends on the nature of exciton polarization. If the lifetime τ_0 is substantially smaller than the exciton spin relaxation time τ_s, we have the simple expressions

$$\mathscr{P}_{\text{lin}} \approx 1 - \tau_0/\tau_s^{(1)}, \quad \mathscr{P}_{\text{circ}} \approx 1 - \tau_0/\tau_s^{(2)}. \tag{3}$$

The times $\tau_s^{(1)}$ and $\tau_s^{(2)}$ may, in general, be quite different.

In accordance with (3), measured values of $\mathscr{P}_{\text{lin}}$ and $\mathscr{P}_{\text{circ}}$ show that, under the conditions prevailing in our

experiment, $\tau_s^{(1,2)} \gtrsim 10\,\tau_0$, i.e., the spin state of the exciton is not appreciably modified during the exciton lifetime. We shall therefore henceforth neglect spin relaxation when we analyze changes in polararization in magnetic fields.

2. Effect of longitudinal magnetic field

Linear polarization. In the longitudinal magnetic field (Faraday geometry, $\mathbf{H} \parallel c$), the emission is found to be depolarized. This occurs since the magnetic field destroys the initial coherence of the $S_Z = \pm 1$ states because of the splitting of the Γ_6 term into two levels with energies

$$E_{1,2} = E_{exc} \pm \hbar\Omega_\parallel/2, \quad \hbar\Omega_\parallel = g_\parallel \mu_0 H_\parallel$$

where μ_0 is the Bohr magneton and $g_\parallel$ is the g-factor of the exciton in the longitudinal fields. The shape of the $\mathcal{P}_{lin}(H_\parallel)$ signal is shown in Fig. 2a. It differs from the classical Lorentz shape: $\mathcal{P}_{lin}(H_\parallel)$ falls rapidly to zero with increasing magnetic field and then changes sign.

Circular polarization. In accordance with the theoretical analysis,[8] the longitudinal magnetic field has practically no effect on the degree of circular polarization for $\tau_0 \ll \tau_s$. The small observed change in the degree of circular polarization is probably due to the field dependence of the spin relaxation of excitons. A similar effect of a magnetic field on the spin relaxation of free carriers and excitons was previously reported in the literature.[11-13]

3. Effects of transverse magnetic field

Linear polarization. a) In a magnetic field at 45° to the plane of polarization of emitted light, the depolarizing effect of the transverse magnetic field (Voigt geometry, $\mathbf{H} \perp c$) is less well defined as compared with the longitudinal field. However, $\mathcal{P}_{lin}(H_\parallel)$ retains most of the features of $\mathcal{P}_{lin}(H_\perp)$ (Fig. 2b). The Γ_6 and Γ_3 states of the exciton are mixed in the transverse field, and the result of this is that the optically inactive state Γ_3 comes into play and the state Γ_6 splits, producing three optically active states, namely, Γ_1, Γ_2, and Γ_3.[10] The energy of Γ_1 does not change as the field increases ($E_1 = E_{exc}$) and the energies of $\Gamma_{2,3}$ shift in opposite directions:

$$E_{2,3} = E_{exc} + {}^1/_2[\Delta \pm (\Delta^2 + \hbar^2\Omega_\perp^2)^{1/2}], \quad \hbar\Omega_\perp = g_\perp \mu_0 H_\perp.$$

Transitions to the state Γ_1 are allowed for $\mathbf{E} \perp \mathbf{H}_\perp$, whilst transitions to the state Γ_2 are allowed for $\mathbf{E} \parallel \mathbf{H}_\perp$. Light polarized linearly at 45° to the direction of $\mathbf{H}_\perp$ excites the coherent superposition of these states. Depolarization of the radiation occurs as a result of the removal of this initial coherence by the magnetic field.

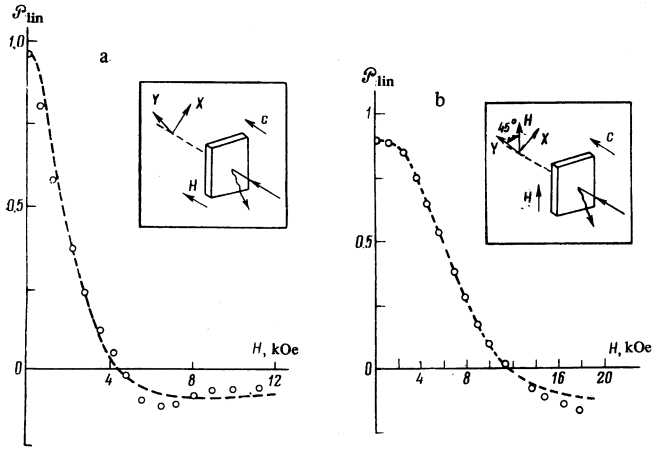

FIG. 2. Degree of linear polarization of exciton emission as a function of the magnetic field under excitation by linearly polarized light. a—Faraday geometry, b—Voigt geometry, $T = 2$ °K. Points—experimental; curves: a—Eq. (14), b—Eq. (16). Inserts illustrate the geometry of the experiment.

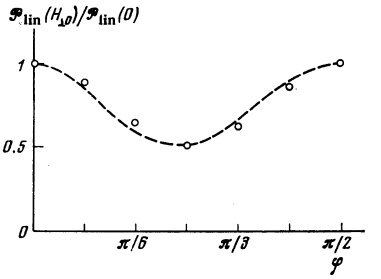

FIG. 3. Degree of linear polarization of exciton emission in a transverse magnetic field as a function of the angle φ between the plane of polarization of the exciting radiation and the direction of the magnetic field $\mathbf{H}_\perp$ for $H_\perp = H_{\perp 0} = 6$ kOe; $T = 2$ °K. Points—experimental, curve—Eq. (12).

b) Since the states Γ_1 and Γ_2 are excited to a different degree for different angles between electric field in the exciting radiation and the direction of the field $\mathbf{H}_\perp$, the behavior of $\mathcal{P}_{lin}(H_\perp)$ depends on the angle φ between $\mathbf{E}$ and $\mathbf{H}_\perp$. When this angle is 0 or $\pi/2$, i.e., when only the state Γ_2 or the state Γ_1 is excited, the degree of polarization does not depend on $H_\perp$. We shall see from the formula given by (12) that, for intermediate values of φ, the polarization $\mathcal{P}_{lin}(H_\perp, \varphi)$ depends on $H_\perp$ to the extent to which φ differs from 0 or $\pi/2$.

Figure 3 shows the angular dependence of $\mathcal{P}_{lin}(H_\perp, \varphi)$ for $H_\perp = 6$ kOe, which corresponds to the half-width of the experimental $\mathcal{P}_{lin}(H_\perp)$ curve in Fig. 2b. It is clear that the depolarizing effect of the field is most strongly defined for $\varphi = 45°$. The total intensity $I(\varphi)$ for $\varphi = 0$ falls by a factor of about two, as compared with its initial value, when the field is varied between 0 and 16 kOe, but for $\varphi = \pi/2$, the intensity is independent of the field.

Excitation with unpolarized light. The form of $I(\varphi)$ indicated above leads to another interesting phenomenon that has been predicted theoretically.[8] In the case of resonance excitation of excitons by natural light in a transverse magnetic field, the reduction in the intensity of radiation with $\mathbf{E} \parallel \mathbf{H}_\perp$ should produce linear polarization of the emitted radiation, with $\mathbf{E}$ lying preferentially in the plane perpendicular to $\mathbf{H}_\perp$. We have, in fact, confirmed this experimentally. To describe this phenomenon, it is convenient to take the coordinate system so that it is related to the direction of the magnetic field $\mathbf{H}_\perp$, and to define the degree of polarization by

$$\mathcal{P}'_{lin} = \frac{I_\perp - I_\parallel}{I_\perp + I_\parallel}, \tag{4}$$

where $I_\perp$ and $I_\parallel$ are the intensities polarized so that $\mathbf{E}\perp\mathbf{H}_\perp$ and $\mathbf{E}\parallel\mathbf{H}_\perp$. As $H_\perp$ increases in the case of excitation with unpolarized light, the degree of polarization $\mathscr{P}'_{\text{lin}}(H_\perp)$ is also found to increase toward a maximum and then falls slowly, as shown in Fig. 4.

It is interesting to consider separately each of the components $I_\perp$ and $I_\parallel$ as functions of the field. The corresponding experimental curves are shown in the insert in Fig. 4. The intensity of radiation with $\mathbf{E}\perp\mathbf{H}_\perp$ is practically independent of the field, whereas the intensity with $\mathbf{E}\parallel\mathbf{H}_\perp$ at first decreases with increasing field and then, after about 16 kOe, it begins to increase slowly. The total intensity at $H_\perp \approx 16$ kOe is reduced by about 25%. We note that, by analogy with the Hanle effect, the appearance of linear polarization in this case is a purely interference effect, unrelated to the preferentially Boltzmann population of one of the magnetic sublevels (Γ_1 or Γ_2) as the field increases (this effect can be observed in the opposite limiting case $\tau_s < \tau_0$, and produces a linear polarization with opposite sign, i.e., preferential polarization with $\mathbf{E}\parallel\mathbf{H}_\perp$).

Circular polarization. Circularly polarized emitted radiation is depolarized in a transverse field (Fig. 5). The behavior of $\mathscr{P}_{\text{circ}}(H_\perp)$ is practically the same as that of $\mathscr{P}_{\text{lin}}(H_\perp)$ for $\varphi = \sphericalangle(\mathbf{E}, \mathbf{H}_\perp) = 45°$. The fact that the function $\mathscr{P}(H_\perp)$ is the same in these two cases is in complete agreement with theoretical predictions. As in the case of linear polarization, the depolarization of circularly polarized emitted radiation in a transverse field is a consequence of the removal by the magnetic field of the initial coherence of the states Γ_1 and Γ_2, resulting from the resonance exciton absorption of the circularly polarized photons.

Theory predicts[8] that a transformation of linear into circular polarization is possible in a transverse field when excitons are excited by radiation that is linearly polarized at 45° to the direction of **H**, and vice versa. We have not been able to confirm this experimentally. Theory also predicts[8] that this effect should be proportional to the exchange splitting constant Δ between exciton states Γ_3 and Γ_6 in zero fields. According to Eq. (2.17) in the paper of Ivchenko *et al.*,[8][13] the absence of the polarization transformation effect can be explained by assuming that $\Delta < 0.01$ meV. We shall therefore assume henceforth that $\Delta = 0$.

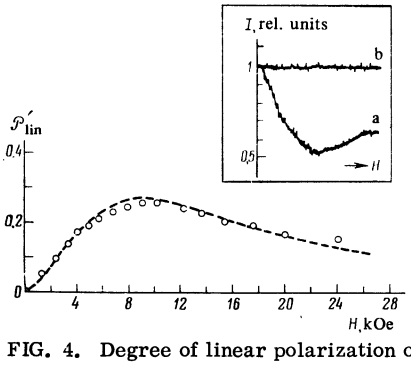

FIG. 4. Degree of linear polarization of exciton emission as a function of the magnetic field under excitation by unpolarized light: $\mathbf{H}\perp c$, $T = 2$ °K. Points—experimental, curve—Eq. (18). Insert shows the intensities of the individual emission components as functions of the magnetic field for $\mathbf{E}\parallel\mathbf{H}$ (a) and $\mathbf{E}\parallel\mathbf{H}_\perp$ (b).

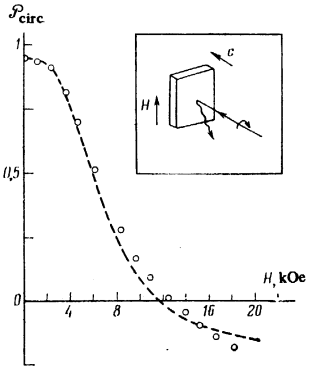

FIG. 5. Degree of circular polarization of exciton emission as a function of the magnetic field under excitation by circularly polarized light. Voigt geometry, $T = 2$ °K. Points—experimental, curve—Eq. (16). Insert shows the geometry of the experiment.

Bound excitons. The two strongest emission lines observed for type II GaSe crystals, i.e., $\lambda_a = 2.097$ eV (5913 Å) and $\lambda_b = 2.089$ (5933 Å) have a number of features (position in the spectrum, strong temperature dependence, corresponding structure in absorption) suggesting that they are emitted by bound excitons.[14] In contrast to the long-wave (relative to the free exciton lines) structure in the spectra of type I crystals, these lines are efficiently excited both under resonance excitation in the region of the $n = 1$ lines of the free exciton and under excitation by light with $\hbar\omega > E_g$.

The insert in Fig. 6 shows the spectrum of bound excitons in type II GaSe crystals under resonance excitation in the region of the $n = 1$ lines of Γ_6. Under these conditions, experiment shows that, when the lines λ_a and λ_b are excited by linearly polarized light, the linear polarization is not conserved whereas, in the case of circularly polarized excitation, the lines are found to be circularly polarized with $\mathscr{P}_{\text{circ}} \approx 0.3$ (λ_a). Under resonance excitation of free excitons, the states λ_a and λ_b are populated through the capture of free excitons by these centers. The absence of linearly polarized λ_a and λ_b under linearly polarized excitation can be explained

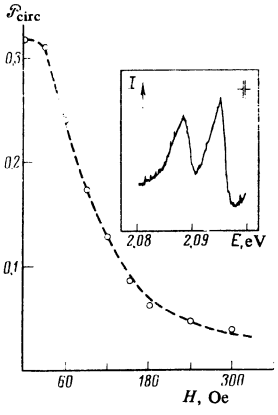

FIG. 6. Degree of circular polarization of emission from a bound exciton, λ_a, as a function of the magnetic field under excitation by circularly polarized light in the region of free-exciton absorption lines. Voigt geometry, $T = 2$ °K. Points—experimental, curve—Eq. (21). Insert shows the emission spectrum from bound excitons; left-hand peak λ_b, right-hand peak λ_a.

by the fact that these states correspond to excitons bound on neutral donors (or acceptors). The resultant dipole moment of electrons (or holes) in such complexes is zero, and the presence of circular polarization under excitation by circularly polarized light is therefore connected with the orientation of the dipole moment of the remaining unpaired hole (electron). This dipole moment precesses in the transverse magnetic field, and this produces depolarization of the emitted radiation.

Figure 6 shows the experimental dependence of the Hanle signal for the line λ_a. The corresponding line profile has the classical Lorentz shape, and can be described by

$$\mathscr{P}_{\text{circ.}}(H_\perp) \sim \frac{1}{1+(H_\perp/\Delta H)^2} \tag{5}$$

with half-width $\Delta H \approx 100$ Oe.

DISCUSSION OF RESULTS AND COMPARISON WITH THEORY

1. Qualitative comparison with phenomenological theory

Before we proceed to a quantitative comparison with theory, let us consider the theoretical predictions[8] in a qualitative fashion. The theory[8] was developed for the following three possible cases:

(a) The phenomenological theory is valid for exciton lifetimes τ_0 much greater than the free exciton momentum relaxation time τ_p and, correspondingly, the time $\tau = (\tau_0^{-1} + \tau_p^{-1})^{-1}$.

(b) The microscopic theory is valid for arbitrary τ_0/τ_p and takes into account the change in the polarization of light in a magnetic field during its propagation in the crystal prior to the formation of the exciton and after its annihilation.

(c) The microscopic theory is valid for highly inhomogeneous broadening over the light absorption length l_d when the change in the polarization of light in a magnetic field during its propagation in the crystal can be neglected.

The results of the phenomenological theory (a) when the exchange splitting of Γ_3 and Γ_6 is $\Delta = 0$ can be obtained by looking upon the exciton as a classical oscillating dipole $\mathbf{P}$ which is initially oriented along the vector $\mathbf{E}$ under resonance excitation with linearly polarized light propagating along the principal Z axis, i.e., $P_\alpha^0 P_\beta^{0*} \sim E_\alpha E_\beta^*$, where $P_{\alpha,\beta}^0$ and $E_{\alpha,\beta}$ are the components of $\mathbf{P}$ and $\mathbf{E}$ along the chosen coordinate axes X, Y ($\alpha, \beta = X, Y$). In a longitudinal magnetic field $H_\parallel$, this dipole will rotate around the direction of $\mathbf{H}_\parallel$ with angular frequency $\Omega_\parallel/2$. In a transverse magnetic field $\mathbf{H}_\perp$, the excited dipole with $\Delta = 0$ will precess with angular velocity $\Omega_\perp/2$. The properties of the band structure ensure that the dipole moment rotates not around the vector $\mathbf{H}_\perp$, as in the case of a classical dipole in the atom, but around the direction perpendicular to $\mathbf{H}_\perp$ and to the optical c-axis, so that the resulting component P_z which appears during this precession does not lead to the polarization of the crystal and does not excite radiation.

The polarization matrix for the emitted light propagating along the Z axis is related to the dipole-moment components as follows:

$$d_{\alpha\beta} \sim \langle P_\alpha P_\beta^* \rangle$$

(the symbol $\langle\ \rangle$ indicates, as usual, that we are taking the average value of $P_\alpha P_\beta^*$). If the probability of radiative recombination of the exciton created at $t = 0$ at time t is $f(t)$, then

$$d_{\alpha\beta} \sim \langle P_\alpha P_\beta^* \rangle \sim \int_0^\infty f(t) P_\alpha(t) P_\beta^*(t)\, dt. \tag{6}$$

When $\tau_0 \gg \tau$, the probability $f(t)$ is determined only by the exciton lifetime:

$$f(t) = \frac{1}{\tau_0} \exp\left(-\frac{t}{\tau_0}\right). \tag{7}$$

This model provides a qualitative explanation of all the main features of polarization in a magnetic field. Its predictions are identical with the results of the phenomenological theory (a) for $\Delta = 0$.

When the exciton is excited by linearly polarized light in a longitudinal magnetic field, the rotation of the dipole moment leads to a reduction in the degree of polarization in accordance with the expression

$$\mathscr{P}_{\text{lin}}(H_\parallel) = \frac{\langle P_Y^2 \rangle - \langle P_X^2 \rangle}{\langle P_Y^2 \rangle + \langle P_X^2 \rangle} = \langle \cos \Omega_\parallel t \rangle = \frac{1}{1+(\Omega_\parallel \tau_0)^2}, \tag{8}$$

where $\mathscr{P}_{\text{lin}}$ is the degree of polarization in the coordinate system X, Y such that the polarization vector of the exciting light is $\mathbf{E} \parallel Y$. In a longitudinal magnetic field, we have the polarization $\mathscr{P}''_{\text{lin}}$ in the coordinate system X', Y' rotated through 45° about the Z axis relative to X, Y:

$$\mathscr{P}''_{\text{lin}}(H_\parallel) = \frac{2\langle P_Y P_X^* \rangle}{\langle P_Y^2 \rangle + \langle P_X^2 \rangle} = -\langle \sin \Omega_\parallel t \rangle = -\frac{\Omega_\parallel \tau_0}{1+(\Omega_\parallel \tau_0)^2}. \tag{9}$$

In a transverse magnetic field $H_\perp = H_X$, the precession in GaSe is such that the dipole moment P_Y remains constant. This is why neither the intensity nor the polarization of the emitted radiation is found to vary under excitation by light polarized in the plane perpendicular to $\mathbf{H}_\perp$. The polarization of the emitted light is also unaffected under excitation by light polarized so that $\mathbf{E} \parallel \mathbf{H}_\perp$ [for $\mathscr{P}_{\text{lin}}(0) = 1$], and the intensity $I_\parallel$ falls by a factor of two in a strong field since

$$I_\parallel(H_\perp) \sim \langle P_X^2 \rangle \sim I_\parallel(0) \left\langle \cos^2\left(\frac{\Omega_\perp t}{2}\right) \right\rangle = \frac{1}{2} I_\parallel(0) \left[1 + \frac{1}{1+(\Omega_\perp \tau_0)^2}\right]. \tag{10}$$

Under excitation by unpolarized light, when two independent dipoles P_X^0 and P_Y^0 are excited, the change in the total intensity in a strong field is reduced by a factor of four due to the change in P_X, and the polarization is preferentially perpendicular to $\mathbf{H}_\perp$. In high fields, the degree of polarization $\mathscr{P}'_{\text{lin}}(H_\perp)$ in the coordinate system attached to the transverse magnetic field $\mathbf{H}_\perp$ is 1/3. It is readily seen that the polarization $\mathscr{P}'_{\text{lin}}(H_\perp)$ will behave in the same way when the crystal is excited by circularly

polarized light or light that is linearly polarized at 45° to the direction of $\mathbf{H}_\perp$. We note that, in the latter case, the polarization $\mathscr{P}_{1\text{in}}(H_\perp)$ in the coordinate system rotated through 45° relative to $\mathbf{H}_\perp$, and attached to the direction of polarization of the exciting radiation, decreases to zero in accordance with the expression

$$\mathscr{P}_{\text{lin}}(H_\perp)=\frac{2\langle P_Y P_X^*\rangle}{\langle P_Y^2\rangle+\langle P_X^2\rangle}=\frac{\langle\cos(\Omega_\perp t/2)\rangle}{I(\Omega_\perp)}=\frac{1}{[1+(\Omega_\perp\tau_0/2)^2]I(\Omega_\perp)}. \quad (11)$$

The circular polarization $\mathscr{P}_{\text{circ}}$ behaves in the same way under excitation by circularly polarized light in a transverse magnetic field, in which $\mathbf{S}$ rotates around Y with angular velocity $\Omega_\perp/2$.

If the angle φ between $\mathbf{E}$ and $\mathbf{H}_\perp$ is neither zero nor $\pi/2$, the precession of the dipole produces a change in both the polarization and the intensity of the emitted radiation. In general, the linear polarization in the coordinate system attached to the vector $\mathbf{E}$ is given by

$$\frac{\mathscr{P}_{\text{lin}}(H_\perp,\varphi)}{\mathscr{P}_{\text{lin}}(0,\varphi)}=\frac{(F_1\cos^2\varphi-F_2\sin^2\varphi)\cos 2\varphi+F_3\sin^2 2\varphi}{F_1\cos^2\varphi+F_2\sin^2\varphi}, \quad (12)$$

where $F_1(H_\perp)$, $F_2(H_\perp)$, and $F_3(H_\perp)$ determine the variation in the emitted intensity in a transverse magnetic field under excitation by linearly polarized light with $\mathbf{E}\parallel\mathbf{H}$, $\mathbf{E}\perp\mathbf{H}_\perp$, and $\mathbf{E}$ at 45° to $\mathbf{H}_\perp$, in accordance with I(2.14), I(2.16), and I(2.17). Equation (12) is quite general and is valid independently of the particular form of $F_i(H_\perp)$ $(i=1,2,3)$. The denominator in (12) controls the dependence of the total intensity I on φ and $H_\perp$.

The oscillating-dipole model thus enables us to achieve a quantitative understanding of all the experimental results, and the expressions for $\mathscr{P}(H)$ obtained with this model are identical with the formulas of the phenomenological theory (a)[8] for $\Delta=0$.

However, this theory does not explain the change in the sign of the polarizations $\mathscr{P}_{1\text{in}}(H_\parallel)$, $\mathscr{P}_{1\text{in}}(H_\perp)$, $\mathscr{P}_{\text{circ}}(H_\perp)$, and the nonmonotonic behavior of $I_\parallel(H_\perp)$ observed experimentally. The more general microscopic theory[8] shows that the change in the sign and the nonmonotonic dependence $\mathscr{P}(H)$ may occur for comparable τ and τ_0. The reason for the change in sign is that excitons with wave vector $\mathbf{k}=\mathbf{q}_0$ are created under resonance excitation of excitons by light, whereas light is emitted by excitons with wave vector $\mathbf{k}=\mathbf{q}$, where $\mathbf{q}_0$ and $\mathbf{q}$ are the wave vectors of the exciting and emitted light, respectively, and $\mathbf{q}_0\neq\mathbf{q}$. If the directions of the exciting and observed light are opposite (as in our experiment), then $q=-q_0$. Therefore, as in the case of the cascade excitation of atoms in gases, the function $f(t)$ in (6) is not a simple exponential. When the excitons take part only in elastic collisions, and the scattering cross section $Q(\vartheta)$ is independent of the scattering angle, i.e., $Q(\vartheta)=Q_0$, then it is readily shown that, for $q\neq q_0$,

$$f(\mathbf{q},t)=\frac{1}{\tau_0-\tau}\left[\exp\left(-\frac{t}{\tau_0}\right)-\exp\left(-\frac{t}{\tau}\right)\right]. \quad (13)$$

Substituting (13) in (6), and taking into account the rotation of the dipole moments, we find that the polarizations obtained in this way as functions of H are nonmonotonic and change sign for certain definite values of H.

Although it enables us to understand the possible reason for the change in the sign of $\mathscr{P}(H)$, this kind of qualitative analysis is not complete or rigorous, and the corresponding formulas differ from those of the microscopic theory[8] even when the change in the polarization of light during its propagation in the crystal and interference effects produced during backward scattering are not taken into account in this theory. The reason for this is that the change in $\langle P_\alpha P_\beta^*\rangle$ in a magnetic field depends not only on the change in the exciton energy spectrum, i.e., the splitting between the exciton Zeeman sublevels, but also on the degree of departure of the frequency ω of the exciting light from precise resonance, since the excitons are exposed to radiation with $|\omega-\omega_{q_0,m}|\lesssim\Gamma=1/2\tau$, where $\hbar\omega_{q_0,m}$ is the resonance frequency corresponding to the intersection of the photon and exciton branches for the spin state m. Under excitation by a broad spectral band with $\Delta\omega\gg\Gamma$, or in the case of large inhomogeneous broadening, there is no explicit function $\mathscr{P}(\omega)$, but integration with respect to ω leads to an additional dependence of $\mathscr{P}$ on the magnetic field, and the simple classical model which takes into account only the nonexponential form of $f(t)$ in (13) becomes unacceptable for $\tau_0\sim\tau$.

2. Quantitative comparison with microscopic theory

Since the experimental shape of $\mathscr{P}(H)$ is close to that predicted by the theory for $\tau_0\sim\tau$, it may be expected that this relation between τ_0 and τ will be valid in our case. To achieve the best quantitative agreement between theory and experiment, we varied the parameters τ_0 and τ. The experimental results were compared with variants (c) and (b) of the theory, which are valid for inhomogeneous broadening along the Z axis at the light absorption depth and in the absence of this broadening, respectively. We sought values of τ_0 and τ ensuring the best agreement with theory simultaneously for all the experimental curves $\mathscr{P}(H)$ obtained for a given specimen. The best agreement was obtained for case (b), i.e., in the absence of inhomogeneous broadening along the Z axis. In particular, the observed intensity $I_\parallel(H_\perp)$ in a strong field (Fig. 4) was obtained only for case (b), in accordance with I(2.14) and I(2.16).

According to I(2.6), the degree of linear polarization of the exciton emission under resonance excitation by linearly polarized light in a longitudinal field, including the Faraday rotation, is given by[8] (for $\tau_0/\tau_s\ll1$, $\Delta=0$)

$$\frac{\mathscr{P}_{\text{lin}}(H_\parallel)}{\mathscr{P}_{\text{lin}}(0)}=\frac{\Phi(\Omega_\parallel,\tau_0,\tau)}{1-\tau/2\tau_0}, \quad (14)$$

where

$$\Phi(\Omega,\tau_0,\tau)=\frac{1}{1+\Omega^2\tau^2}\left(\frac{1-\Omega^2\tau_0\tau}{1+\Omega^2\tau_0^2}-\frac{1}{2}\frac{\tau}{\tau_0}\frac{1-\Omega^2\tau^2}{1+\Omega^2\tau^2}\right). \quad (15)$$

According to I(2.14) and I(2.15), the degree of linear polarization of the exciton emission under resonance excitation of the crystal by light with linear polarization at 45° to the direction of $\mathbf{H}_\perp$, and the degree of circular polarization under excitation by circularly polarized light, are given by

$$\frac{\mathscr{P}_{\text{lin}}(H_\perp)}{\mathscr{P}_{\text{lin}}(0)}=\frac{\mathscr{P}_{\text{circ}}(H_\perp)}{\mathscr{P}_{\text{circ}}(0)}=\frac{\Phi(\Omega_\perp/2,\tau_0,\tau)}{V(\Omega_\perp,\tau_0,\tau)+1-\tau/2\tau_0}, \quad (16)$$

where $\Phi(\Omega, \tau_0, \tau)$ is given by (15) and

$$V(\Omega, \tau_0, \tau) = \left(1-\frac{1}{2}\frac{\tau}{\tau_0}\right)\left[1-\frac{1}{2}\frac{1}{(1+\Omega^2\tau^2)^{1/2}}\right]+\left[1-\frac{(1+\Omega^2\tau^2)^{1/2}}{2}\right]\Phi(\Omega, \tau_0, \tau). \quad (17)$$

Linear polarization in the plane perpendicular to $\mathbf{H}_\perp$ appears when the excitons are exposed to natural light in a transverse magnetic field. According to I(2.14) and I(2.15a), we have

$$\frac{\mathscr{P}'_{\text{lin}}(H_\perp)}{\mathscr{P}_{\text{lin}}(0)} = \frac{V(\Omega_\perp, \tau_0, \tau)-(1-\tau/2\tau_0)}{V(\Omega_\perp, \tau_0, \tau)+1-\tau/2\tau_0} \quad (18)$$

The dashed curves in Figs. 2, 4, and 5 correspond to (14), (16), and (18) with $\tau_0 = 1.6\times10^{-11}$ sec and $\tau = 0.4\times10^{-11}$ sec. To determine $\Omega_\parallel$ and $\Omega_\perp$, we used $g_\parallel = 2.7$ and $g_\perp = 1.9$ for the exciton.[10] It is clear that the theoretical predictions are in satisfactory agreement with the experimental data on $\mathscr{P}(H)$.

The polarization of radiation emitted by aligned excitons as a function of the angle φ between $\mathbf{E}$ in the exciting radiation and $H_\perp$ is in good agreement with (12). The theoretical results calculated from this formula are indicated in Fig. 3 by the dashed curve. The values of F_1, F_2, and F_3 were determined experimentally, and the field $H_{\perp 0}$ was chosen so that $\mathscr{P}_{\text{lin}}(H_{\perp 0}, \varphi)/\mathscr{P}_{\text{lin}}(0, \varphi)|_{\varphi=45^\circ} = 0.5$.

Equations (14), (16), and (18) were obtained under certain definite assumptions with regard to the exciton parameters reflecting the kinetic properties of excitons and the light-exciton interaction. The most stringent of these conditions, which enables us to ignore the light-exciton interaction, and in particular, neglect the reemission of light, is condition I(1.21):

$$\omega_{LT}\tau \ll (\omega_{q_0}\tau_0)^{-1}. \quad (19)$$

This enables us to neglect the repeated creation of excitons by the emitted light. In this expression, $\hbar\omega_{LT}$ is the longitudinal-transverse splitting and $\hbar\omega_{q_0} = \hbar^2 q_0^2/2m_0$ is the kinetic energy of an exciton with momentum $\hbar\mathbf{q}_0$.

The experimental value ω_{LT} for the Γ_6 exciton in GaSe is not accurately known, but is probably very small.[10] Since the absorption coefficient is $\alpha \approx 1000$ cm^{-1} [15] for the Γ_6 exciton in GaSe, it follows that $\hbar\omega_{LT} \approx 0.005$ meV. The inequality given by (19) is well satisfied for these values of ω_{LT} if the translational mass of the exciton along the c-axis is $m_e = 0.5\,m_0$ [16] and the exciton wave vector is $q_0 = 2\pi n/\lambda = 3.2\times10^5$ cm^{-1} ($n = 3$ [17] is the refractive index of GaSe and λ is the wavelength corresponding to the energy of the exciton transition).

The theoretical analysis[8] also assumes the condition for the validity of the kinetic equation, i.e.,

$$\omega_{q_0}\tau \gg 1 \quad \text{or} \quad q_0 \gg l_e^{-1}, \quad (20)$$

where $l_e = \hbar q_0 \tau/m_e$ is the exciton mean free path. For the above values of m_e, q_0, and τ, the quantities q_0 and l_e^{-1} turn out to be of the same order. However, satisfactory agreement between theory and experiment enables us to extrapolate the theoretical prediction to the case $q_0 l_e \sim 1$ as well. We note that, in the theory of highly doped semiconductors with free-carrier concentrations corresponding to an analogous situation, the results obtained on the basis of the kinetic equation are also in satisfactory agreement with experiment.

Theory[8] predicts that the nonmonotonic form of $\mathscr{P}(H)$ and the change in the sign of $\mathscr{P}(H)$ for certain definite values of H occur only under resonance excitation and when τ_0 and τ are comparable in magnitude. The usual excitation of exciton luminescence by light with energy exceeding the band gap does not lead to this effect even for $\tau_0 \sim \tau$. Excitation by light with $\hbar\omega > E_g$ can produce only free electrons and holes, or "hot" excitons. The necessary condition for the observation of exciton luminescence is that the excitons relax to the bottom of the exciton band in the neighborhood of the point with momentum $\sim\hbar\mathbf{q}$. This relaxation is not accompanied by the appearance of a preferential direction for the exciton momentum at the bottom of the band and, consequently, when $\tau_0 \sim \tau$, the functions $\mathscr{P}_{\text{lin}}(H)$ and $\mathscr{P}_{\text{circ}}(H)$ have the usual monotonic character. This is one of the reasons why the influence of exciton-momentum relaxation was not observed previously in experiments on the optical orientation of excitons in GaSe.[2,13] A similar situation was encountered in experiments on the alignment of excitons in CdSe crystals[18] and during the excitation of exciton emission by light with energy exceeding the exciton ground-state energy by the energy of $2LO$ phonons for which the usual Lorentz shape was observed for $\mathscr{P}_{\text{lin}}(H_\parallel)$ with $\tau_0 \approx 10^{-11}$ sec.

3. Bound excitons

When a bound exciton is formed as a result of capture of free excitons by neutral acceptors (donors) under resonance excitation, i.e., the process has a cascade character, and the free and bound exciton lifetimes are comparable, the function $\mathscr{P}_{\text{circ}}(H_\perp)$ is nonmonotonic for bound excitons, as is the case of cascade excitation of atoms. However, experiment indicates a Lorentz shape for $\mathscr{P}_{\text{circ}}(H_\perp)$, and this function falls in much weaker fields than for free excitons. In such fields, the spins in the free excitons do not succeed in precessing during the lifetime, and $\mathscr{P}_{\text{circ}}(H_\perp)$ is determined only by the precession of the electron (hole) spin in the bound exciton:

$$\mathscr{P}_{\text{circ}}(H_\perp) = \frac{\mathscr{P}_{\text{circ}}(0)}{1+(\Omega_\perp{}^e T_D)^2}, \quad (21)$$

where

$$\hbar\Omega_\perp{}^e = g_\perp{}^e\mu_0 H_\perp, \quad T_D^{-1} = \tau_D^{-1}+\tau_{Ds}^{-1};$$

in which τ_D and τ_{Ds} are the lifetime and spin-relaxation time of a bound exciton. The broken curve in Fig. 6 represents (21) for $T_{Ds} \approx 10^{-9}$ sec and $g_\perp^e \approx 1$.

If we suppose that the spins of the carriers bound in the exciton do not succeed in losing their correlation in the time between the creation of the exciton by light and its capture by the corresponding defect, the result

$$\mathscr{P}_{\text{circ}}(0) = \frac{\tau_{Ds}}{\tau_D+\tau_{Ds}} \approx 0.3 \quad (22)$$

can be used to obtain the separate values $\tau_D = 3\times10^{-9}$ sec and $\tau_{Ds} = 1.5\times10^{-9}$ sec. Since the free-exciton lifetime is $\tau_0 \sim 10^{-11}$ sec, it is clear that τ_0 and τ_D differ by more than two orders of magnitude.

CONCLUSIONS

We have carried out an experimental investigation of optical orientation and alignment of excitons under resonance excitation in GaSe crystals. We have shown that the observed properties of polarized luminescence emitted by oriented and aligned excitons in an external magnetic field can be satisfactorily explained within the framework of the theory[8] that takes into account the exciton momentum distribution produced during the reradiation of light under resonance excitation. The experimental results can also be qualitatively described in terms of oscillating exciton dipoles. It follows that the polarized-luminescence spectrum emitted by excitons can, at least in principle, be used to obtain information not only about the energy structure of the exciton states (levels) and exciton lifetimes, but also about their kinetic properties.

GaSe crystals are, in a sense, unique in that they can be used to investigate resonance exciton emission under resonance excitation. This is connected with the fact that there is no strong background of scattered exciting light. This, in turn, may be connected with the layered structure of the crystal and, in particular, the high optical quality of the surface produced by cleaving the crystals along the layer planes, which strongly reduces the intensity of diffuse scattering. For example, strong scattered-light background has prevented the reliable detection of exciton luminescence from A^2B^6 crystals under resonance excitation under similar conditions. It would be interesting to extend the range of materials for experiments on polarized luminescence of excitons under resonance excitation, because many of the features of orientation and alignment observed in GaSe are indicated by the theory as being quite general and maybe observable in the exciton spectra of other semiconductors.

It is important to note that the advantage of GaSe lies in the fact that the exciton-photon interaction for the triplet excitons $n=1$, $S=1$ (Γ_6) is small. The low value of the absorption coefficient at the frequency of this transition is connected with the fact that the excitation of this exciton is generally forbidden when the spin-orbit interaction is ignored and the separation between the $S=1$ level and the level corresponding to the allowed singlet exciton ($S=0$) in GaSe is sufficiently large. This enables us to neglect polariton effects, for example, the reradiation of light.

In crystals with stronger exciton-photon interaction, the above theory must be suitably modified. In particular, the reabsorption of light should substantially reduce the degree of polarization of radiation emitted under resonance excitation by polarized light.

[1)] Polarization of exciton luminescence is understood to mean polarization due to the polarization of the exciting light.

[2)] This structure must not be confused with the structure due to the exchange interaction. In accordance with the excitation ($E \perp c$) and detection conditions, the Γ_4 excitons are not seen in the spectrum of Fig. 1. The corresponding structure is found to be present in emission spectra if the directions of excitation and detection depart appreciably from the normal to the crystal surface.

[3)] Formulas taken from this paper will be indicated by I followed by the number of the equation; for example, I(2.17).

[1] E. F. Gross, A. I. Ekimov, B. S. Razbirin, and V. I. Safarov, Pis'ma Zh. Eksp. Teor. Fiz. **14**, 108 (1971) [JETP Lett. **14**, 70 (1971)].

[2] Yu. P. Veshchunov, B. P. Zakharchenya, and E. M. Leonov, Fiz. Tverd. Tela (Leningrad) **14**, 2678 (1972) [Sov. Phys. Solid State **14**, 2312 (1973)].

[3] G. L. Bir and G. E. Pikus, Pis'ma Zh. Eksp. Teor. Fiz. **15**, 730 (1972) [JETP Lett. **15**, 516 (1972)]; Zh. Eksp. Teor. Fiz. **64**, 2210 (1973) [Sov. Phys. JETP **37**, 1116 (1974)].

[4] A. Bonnot, R. Planel, and C. Benoit à la Guillaume, Phys. Rev. B **9**, 690 (1974).

[5] B. S. Razbirin, V. P. Mushinskiĭ, M. I. Karaman, A. N. Starukhin, and E. M. Gamarts, Pis'ma Zh. Eksp. Teor. Fiz. **22**, 203 (1975) [JETP Lett. **22**, 94 (1975)].

[6] B. S. Razbirin, V. P. Mushinskiĭ, M. I. Karaman, A. N. Starukhin, and E. M. Garmarts, Izv. Akad. Nauk SSSR Ser. Fiz. **40**, 1872 (1976).

[7] S. A. Permogorov, Ya. V. Morozenko, and B. A. Kazennov, Fiz. Tverd. Tela (Leningrad) **17**, 2970 (1975) [Sov. Phys. Solid State **17**, 1974 (1976)].

[8] E. L. Ivchenko, G. E. Pikus, B. S. Razbirin, and A. N. Starukhin, Zh. Eksp. Teor. Fiz. **72**, 2230 (1977) [Sov. Phys. JETP **45**, 1172 (1977)].

[9] J. M. Daniels, Rev. Sci. Instrum. **38**, 284 (1967).

[10] E. Mooser and M. Schlüter, Nuovo Cimento B **18**, 164 (1973).

[11] R. R. Parsons, Can. J. Phys. **49**, 1850 (1971).

[12] V. L. Berkovits, A. I. Ekimov, and V. I. Safarov, Zh. Eksp. Teor. Fiz. **65**, 346 (1973) [Sov. Phys. JETP **38**, 169 (1974)].

[13] F. Minami, Y. Oka, and T. Kushida, J. Phys. Soc. Jpn. **41**, 100 (1976).

[14] M. I. Karaman, V. P. Mushinskiĭ, B. S. Razbirin, A. N. Starukhin, and S. S. Chekoĭ, Fiz. Tekh. Poluprovodn. **6**, 412 (1972) [Sov. Phys. Semicond. **6**, 356 (1972)].

[15] J. Halpern, Proc. Eighth Intern. Conf. on Physics of Semiconductors, Kyoto, 1966, in: J. Phys. Soc. Jpn. **21**, Suppl., 180 (1966).

[16] G. Ottaviani, C. Canali, F. Nava, P. Schmid, E. Mooser, R. Minder, and I. Zschokke, Solid State Commun. **14**, 933 (1974).

[17] G. A. Akhundov, S. A. Mussev, A. E. Bakhyshev, N. M. Gasanly, and L. G. Musaeva, Fiz. Tekh. Poluprovodn. **9**, 142 (1975) [Sov. Phys. Semicond. **9**, 94 (1975)].

[18] M. Nawroski, R. Planel, and C. Benoit à la Guillaume, Phys. Rev. Lett. **36**, 1343 (1976).

Translated by S. Chomet