Excitons bound to phosphorus impurity atoms in germanium

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Magnetopiezospectroscopic methods were used in a study of excitons bound to phosphorus impurity atoms in crystalline germanium. The splitting of an excited "electron" term $\{\Gamma_1, \Gamma_5; \Gamma_8\}$ of an exciton bound to a donor (ED) was attributed to the interaction between electrons and a hole. A model accounting for the observed splitting was proposed. New "hole" excited states of ED were detected. The constants representing the interaction of ED with a magnetic field in weakly deformed germanium were determined. It was found that uniaxial deformation of germanium by pressures of 10–80 MPa shifted nonlinearly some of the ED levels with pressure and was accompanied by a major change in the corresponding oscillator strengths and g factors. This was explained qualitatively by a modification of the ED states due to splitting of the valence band.

1. INTRODUCTION

Bound excitons and many-particle exciton-impurity complexes have been the subject of many experimental and theoretical investigations, the main results of which can be found in a number of reviews (see, for example, Refs. 1–3). However, the problem of bound excitons and of many-particle exciton-impurity complexes is not yet fully resolved.

An important stage in the development of the ideas on bound excitons and many-particle exciton-impurity complexes has been the development of a shell model.[4] According to the shell model, electrons and holes in bound excitons and in many-particle exciton-impurity complexes occupy consecutively electron and hole shells in accordance with the Pauli principle. It is assumed that in the zeroth approximation the shells can be regarded as linear combinations of antisymmetrized products of one-particle "self-consistent" wave functions transforming in accordance with irreducible representations of the point group of an impurity center. If we assume that the wave function of the first electron (hole) shell is constructed from one-particle functions which are not orthogonal to one another, one of which is close to a donor (acceptor) and the other much more extended in space,[5] we find that the shell model does indeed explain the bulk of the experimental results known at present. Nevertheless, the representation of the states of many-particle exciton–impurity complexes by antisymmetrized products cannot be regarded as correct even in the zeroth approximation, because this approach ignores a large part of the correlation energy. This is evident, for example, from a comparison of an ED complex[1)] with a D^- center.[6] (In our opinion the electron structure of the D^- centers is in many respects analogous to the first electron shell of E_kD.) It is shown in Ref. 7 that the correlation energy represents more than 50% of the energy of the ground state of a D^- center.

We should mention also here numerical calculations[8–10] of the ground and excited states of E_kD complexes. These calculations were carried out in fact ignoring the main principles of the shell model. They demonstrated that E_kD may have the ground state as well as a series of excited stationary states. However, the precision of the variational procedures employed in these investigations was insufficient for using the results in the interpretation of experiments.

We thus see that in spite of the important role played by the shell model and of the model used in numerical calculations of the terms of E_kD, the main methods for the investigation of bound excitons and many-particle exciton-impurity complexes are still optical. The high information capacity of optical methods is due to the fact that absorption and recombination radiation lines of bound excitons and of many-particle exciton-impurity complexes are extremely narrow ($\sim 10\,\mu$eV for silicon and $\sim 25\,\mu$eV for germanium), so that it is possible to determine very accurately the positions of these lines in the spectra, their intensities and the degree of polarization, as well as the dependences of these parameters on external perturbations.

Excitons bound to shallow donors in germanium have been investigated before.[11–16] It has been established that in addition to the ground state with the Γ_1 symmetry, an ED complex has a number of excited states: an s-like "electron" state of the Γ_5 symmetry[11–13]; an electron state due to the capture of an exciton by a donor which is in an excited Γ_5 state[14]; a p-like hole state with the Γ_5 symmetry[15]; several metastable states of unknown nature.[16] We shall show that there may be also additional states of ED.

The present paper describes an investigation of excitons bound to phosphorus impurity atoms in germanium. We investigated the spectra of the photoconductivity current and of the Hall emf in the case of resonant photoexcitation of ED, and also recombination radiation spectra of samples subjected both to uniaxial compression and a static magnetic field.

2. EXPERIMENTAL METHOD

Phosphorus-doped germanium crystals were pulled from molten germanium in a stream of pure hydrogen in accordance with the Czochralski method. Phosphorus was selected as the impurity because then the grown crystals did not have a significant number of other donors. Samples used in the recombination radiation and photoconductivity investigations were cut along the [001] and [111] crystallographic directions to form parallelepipeds with the dimensions $2\times2\times20$ mm. The orientation along the [001] direction was accurate to within 13′. The method used to create a homogeneous deformation and a magnetic field (in

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the Voigt configuration) was described in Ref. 14. A sample was placed in a helium bath of a cryostat. Pumping of liquid helium vapor made it possible to vary the helium bath temperature from 4.2 K to below the λ point. In those cases when it was necessary to raise the temperature of a sample above 4.2 K this was done by altering the power of the radiation of a laser used for the purpose of excitation. A sample was placed in a glass tube sealed hermetically from above by a plunger through which a pressure was applied. Evaporation of liquid helium forced it out of the tube. This reduced seriously the thermal coupling between the sample and the helium bath. The sample was heated by the absorption of the energy of exciting radiations; the temperature of the sample was not monitored.

In the recombination radiation studies a sample was excited using an LG-106M-1 argon laser and chopping mechanically the radiation from this laser at a frequency of 72 Hz. A spectroscopic analysis of the recombination radiation excited in this way was carried out by a method described in Ref. 14. This radiation was recorded using a liquid-nitrogen-cooled photoresistor.[17]

In the study of the photoconductivity and Hall effect spectra a sample was excited with modulated radiation from a tungsten ribbon lamp with an output power of 60 W, which was passed first through a double high-luminosity monochromator of the CDL-1 type. The modulated part of the photosignal generated in the sample was amplified, subjected to lock-in detection, and recorded. The method used in the study of the photoconductivity was described in greater detail in Ref. 16.

3. "ELECTRON" EXCITED STATES OF AN EXCITON-DONOR COMPLEX

Figure 1a shows the zero-phonon components of the recombination radiation (luminescence) spectrum of excitons bound to phosphorus impurity atoms. A similar spectrum was reported in Ref. 12. The only difference is that in the spectrum shown in Fig. 1 there is no weak band, reported in Ref. 12, between the luminescence bands labeled γ_1^2 and γ_1^3. The bands α_1 and γ_1^i in Fig. 1 represent radiative decay of bound excitons which are respectively in the ground $\{2\Gamma_1;\Gamma_8\}$ and excited $\{\Gamma_1, \Gamma_5; \Gamma_8\}$ states. A neutral donor is then created in the states Γ_1 and Γ_5. This is confirmed by the observation that, for example, when samples are cooled below 2 K the γ_1 bands practically disappear from the spectrum, whereas the intensity of the α_1 bands changes only slightly.

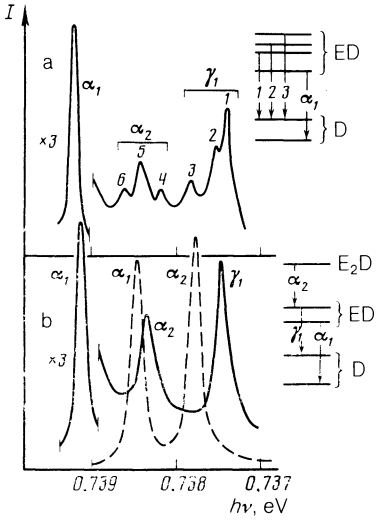

FIG. 1. Luminescence spectrum of many-particle exciton-impurity complexes in Ge:P. Phosphorus concentration 3.5×10^{14} cm^{-3}. a) $P=0$, $T=4.2$ K; b) $P\|[001]$; the continuous curve represents the results obtained at $P=30$ MPa at $T=4.2$ K and the dashed curve corresponds to $P=105$ MPa, $T=2$ K. The optical transition schemes are also included. No correction was made for the monochromator transmission, so that the ratios of the intensities of the bands α_1, α_2, and γ are distorted.

The presence of several γ_1 bands in the luminescence spectrum is due to the splitting of the $\{\Gamma_1, \Gamma_5; \Gamma_8\}$ term because of the interaction of charge carriers in ED. The magnitude of this splitting is comparable with the energy separation between the ED terms (Fig. 1). The luminescence represented by the α_2^i bands in Fig. 1 is due to decay of E_2D exciton complexes: $E_2D \rightarrow ED + h\nu$. This creates ED in one of its excited states $\{\Gamma_1, \Gamma_5; \Gamma_8\}$ (as demonstrated in Fig. 1). It should be pointed out that the luminescence band α_2^5 reported in Ref. 12 and denoted there by X was not identified.

We investigated the luminescence spectra in greater detail than in Ref. 14 and we used samples deformed along the [001] direction to identify the interaction of carriers in ED responsible for the observed splitting of the $\{\Gamma_1, \Gamma_5; \Gamma_8\}$ term. Compression of germanium along this direction should not alter significantly the interaction of electrons in ED, because this deformation should split only the valence band and not the conduction band. (Under our experimental conditions the splitting of the conduction band by a pressure of $P=30$ MPa did not exceed 30 μeV.)

Figure 1b shows typical luminescence spectra of excitons bound to phosphorus impurity atoms in deformed germanium. A comparison of the spectra in Figs. 1a and 1b demonstrates that the deformation results in a major modification of the luminescence spectrum. First of all, even at low pressures ($P\sim25$ MPa) the fine structure of the γ_1 and α_2 luminescence bands disappears. Next, as the pressure is increased, the intensity of the band α_2 rises rapidly and at $P=50$ MPa it becomes comparable with the intensity of the α_1 band. The band α_2 grows from the band α_2^5, so that the α_2^5 band may be attributed to decay of E_2D complexes. At $T=2$ K under a pressure of $P=100$ MPa only two narrow bands α_1 and α_2 of comparable intensity remain in the luminescence spectrum. Disappearance of the fine structure of the α_1 and γ_1 bands shows that in the excited $\{\Gamma_1, \Gamma_5; \Gamma_8\}$ state of ED in undeformed germanium the interaction between electrons and holes predominates over the interaction between the Γ_1 and Γ_5 electrons, contrary to the assumptions made in Refs. 9 and 18.

This is in good agreement with the Zeeman splitting spectra of the α_2 band obtained for crystals compressed along the [001] ($\mathbf{B}\|\mathbf{P}$) direction. According to Ref. 14, under these conditions the α_2 band should split into four components, as indeed found in the range $P<60$ MPa. At $P\approx80$ MPa the electron and hole g factors become equal (see Sec. 4 below) and only three components remain in the spectrum (Fig. 2). The g_e and g_h factors determined from the data of Fig. 2 are ≈1.65.

In an analysis of the fine structure of the γ_1 luminescence band emitted by undeformed germanium we shall consider only the interaction between electrons and a hole. Fol-

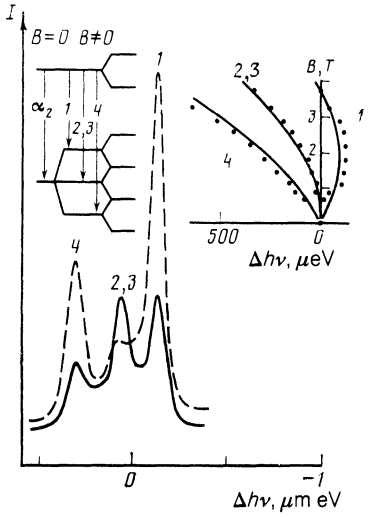

FIG. 2. Zeeman splitting of the zero-phonon α_2-NP luminescence lines of E_2D in a sample of Ge:P compressed along the [001] axis by $P = 81$ MPa. Voigt configuration ($\mathbf{B}\|[001]$), $B = 2.24$ T, $T = 2$ K. Phosphorus concentration 3.5×10^{14} cm^{-3}. The dashed curve is the spectrum of the luminescence polarized along [001] and the continuous curve represents the luminescence polarized at right-angles to [001]. The energies are measured from the α_2 band in the absence of a magnetic field. The optical transition scheme is given on the left ($g_e = g_h$). The inset on the right gives the dependences of the spectral positions of the Zeeman components of the zero-phonon α_2-NP luminescence bands on the magnetic field applied at $T = 2$ K when $P = 85$ MPa.

lowing Ref. 14, we shall assume that a Γ_8 hole interacts mainly with a Γ_5 electron. The interaction between the Γ_5 electron and the Γ_8 hole in ED, considered allowing for the valley-orbit interaction but ignoring the exchange interaction,[2)] is described by the following matrix:

$$H^{eh}=\Delta_{vo}I\otimes I_4+\Delta_1\sum_{i,j=xy,yz,xz}[L_iL_j]\otimes[J_iJ_j]+\sum_{i=x,y,z}\left(\Delta_2L_i\otimes J_i+\Delta_3L_i\otimes J_i^3+\Delta_4\left(L_i^2-\frac{2}{3}\right)\otimes J_i^2\right)+\Delta_5\sum_{\substack{i,j,k=xyz,\\ yzx,zxy}}R_i\otimes[J_jJ_k], \quad (1)$$

where I, L_i, R_x, R_y, and R_z are four-dimensional matrices written down in the valley-orbit basis x, y, z, and 1:

$$I=\begin{pmatrix}0&0&0&0\\0&0&0&0\\0&0&0&0\\0&0&0&1\end{pmatrix},\quad R_x=\begin{pmatrix}0&0&0&1\\0&0&0&0\\0&0&0&0\\1&0&0&0\end{pmatrix},$$

$$R_y=\begin{pmatrix}0&0&0&0\\0&0&0&1\\0&0&0&0\\0&1&0&0\end{pmatrix},$$

$$R_z=\begin{pmatrix}0&0&0&0\\0&0&0&0\\0&0&0&1\\0&0&1&0\end{pmatrix},\quad L_i=\begin{pmatrix}l_i&0\\0&0\end{pmatrix};$$

J_i and l_i are, respectively, four- and three-dimensional matrices of the angular momentum[5]; I_n is an n-dimensional unit matrix; Δ_{vo} is the valley-orbit splitting constant; Δ_i are the constants representing the Coulomb e-h interaction. We can describe the e-h interaction in weakly deformed crystals by supplementing the matrix of Eq. (1) with the deformation matrix $H(\varepsilon)$ (Ref. 5). The solution of the equation

$$|H^{eh}+H(\varepsilon)-\lambda I|=0$$

for given values of Δ_i determines completely the splitting of the term $\{\Gamma_1, \Gamma_5; \Gamma_8\}$ and makes it possible to synthesize part of the luminescence spectrum corresponding to the γ_1 and α_1 transitions allowing for the degeneracy populations of the levels.[5] Interaction of an electron with a hole in germanium is also considered in Ref. 18, where the e-h interaction operator is described by

$$H^{eh}=\sum_{i=1}^{4}\frac{\Delta_{cr}}{2}\left(J_{z_i}^2-\frac{5}{4}\right)$$

(summation over the valleys), i.e., it is assumed that an electron in a valley interacts with a hole, in the same way as in a free exciton. This approach is equivalent to inclusion in Eq. (1) of only the first two and last terms, if we assume that $\Delta_1 = -2\Delta_{cr}/3$ and $\Delta_5 = \Delta_{cr}/3$. It is shown in Ref. 18 that the $\{\Gamma_1, \Gamma_5; \Gamma_8\}$ term splits under the action of the Coulomb e-h interaction into three components with energies 0 and $\pm\Delta'$, where $\Delta = \Delta_{cr}/2$. If we assume that $\Delta_{cr} \approx \Delta_{cr}^{FE}$ (here, $\Delta_{cr}^{FE} = 1.05$ meV is the crystal splitting of the ground state of a free exciton), we find that the value of Δ_1 is close to 0.6 meV so that the corresponding Δ_1 term in Eq. (1) predominates. The good agreement between the calculated and experimental spectra at $P = 0$ and $P \neq 0$ is obtained if the following values of the constants (in microelectron-volts) are substituted in Eq. (1):

$\Delta_{vo}=-1150$, $\Delta_1=300$, $\Delta_2=100$, $\Delta_3=-53$, $\Delta_4=0$, $\Delta_5=-100$.

If the values of these constants are altered by $\pm 10\,\mu$eV, the agreement is much poorer. It should be noted that the value of the constant Δ_1 differs approximately by a factor of 2 from that predicted in Ref. 18. It should be stressed that the e-h interaction described by the last term in Eq. (1) and responsible for the mixing of the Γ_1 and Γ_5 electron states has little effect on the splitting of the $\{\Gamma_1, \Gamma_5; \Gamma_8\}$ term and this can be ignored in a qualitative analysis.

4. "HOLE" EXCITED STATES OF AN EXCITON-DONOR COMPLEX

Excitons bound to neutral donors in germanium have a complex system of "hole" excited states. These states can be investigated conveniently using the spectral distribution of the photoconductivity current J (Ref. 16), because the intensities of the individual bands in the photoconductivity spectra (in contrast to luminescence spectra) depend solely on the dipole moments of the transitions in a crystal to the states corresponding to these bands. Typical photoconductivity spectra are presented in Fig. 3. The Hall effect was investigated under dc conditions and the spectra of the Hall emf U_H were found to be practically identical with the photoconductivity spectra.

Before interpretation of the individual bands in the photoconductivity spectra (Fig. 3), we shall consider first the characteristic features of the photoconductivity and Hall spectra observed by us. The photoconductivity investigated by us appears as a result of a resonant photoexcitation of ED

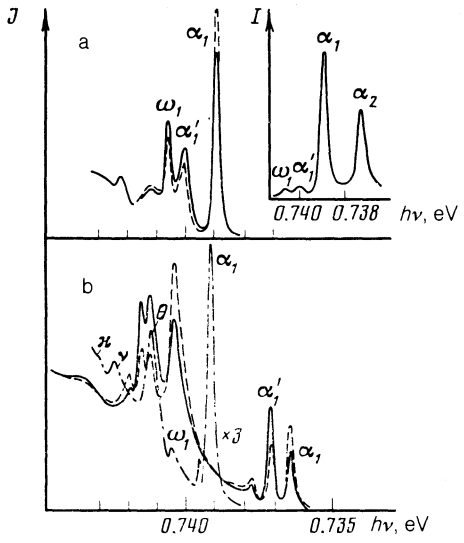

FIG. 3. Spectra of the photoconductivity current J obtained at $T = 4.2$ K for germanium crystals doped with phosphorus in a concentration of 5×10^{15} cm $^{-3}$. The dashed curve is used for the photoconductivity spectra excited by radiation polarized along the deformation axis, whereas the continuous curve represents the case when the radiation was polarized at right-angles to the deformation axis. a) Crystal compressed along [001] by 39 MPa. The inset shows the low-temperature luminescence spectrum of the same sample compressed by 43.6 MPa at $T \approx 7$ K. b) Crystal compressed along [111] by a pressure of 79 MPa. The chain curve represents the spectrum of the crystal in the undeformed state.

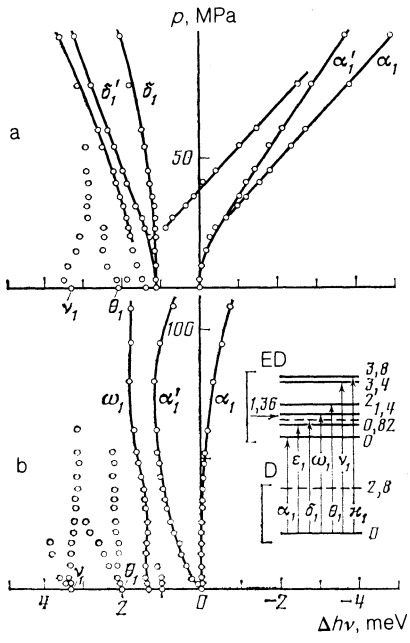

FIG. 4. Dependences of the spectral positions of the photoconductivity bands of germanium doped with phosphorus in a concentration of 5×10^{15} cm $^{-3}$ on the pressure applied at $T = 4.2$ K: a) $\mathbf{P} \| [111]$; b) $\mathbf{P} \| [001]$. The inset shows a scheme of optical transitions that create ED (in the absence of pressure). The excited electron states are represented by dashed lines. The higher dashed line corresponds to states of energies 1, 1.14, and 1.4 meV. The numbers on the right are the energies (in millielectron volts) of the levels measured from the ground state. The arrow on the left corresponds to the exciton energy band edge.

by electrons generated as a result of nonradiative Auger decay of ED. In view of the resonant nature of the photoexcitation the ED complexes are represented in the photoconductivity spectra by sharp peaks against the background of a step due to the D^- centers with a fairly steep red edge near the ω_1 band (Fig. 3).[16] Holes should appear in the valence band as a result of photoexcitation of the D^- centers. Therefore, we can expect an investigation of the Hall effect to provide the basis for distinguishing these two mechanisms of excitation of the photoconductivity. However, as pointed out already, the photoconductivity and Hall effect spectra are practically identical, indicating n-type conduction in both cases. In weak magnetic fields ($B < 10^{-2}$ T) the Hall effect behaves normally: $U_H(\mathbf{B}) = -U_H(-\mathbf{B})$, and so on. In fields $B > 10^{-2}$ T the photoconductivity and Hall effect signals decrease on increase in B (approximately by an order of magnitude when B is increased to ≈ 1.5 T). It follows that the conduction in our samples is of nonband nature (under the selected experimental conditions) and is probably associated with the Hubbard conduction in the D^- band.[19]

We shall now turn back to Fig. 3, which shows the photoconductivity spectrum also recorded at $P = 0$ MPa. The spectrum is similar to that reported in Ref. 16. The θ_1, ν_1 and $\varkappa_1$ bands (denoted by α, β, and γ in Ref. 16) in the photoconductivity spectrum are attributed in Ref. 16 to transient excited states of EH. The band ω_1 has not been interpreted. Additional information on ED was obtained by a detailed investigation of the spectral density of the photoconductivity and of the Zeeman luminescence spectra of samples subjected to pressure along the [001] and [111] directions. Typical photoconductivity spectra due to resonant excitation of ED with radiation polarized parallel or perpendicular to the compression axis are shown in Fig. 3.

Figure 4 shows the pressure dependences of the spectral positions of the peaks, plotted on the basis of the spectral dependences of the photoconductivity. The band α_1 corresponds to Auger decay of bound excitons photoinduced in a crystal in the ground state. Compression of samples along the [001] and [111] directions splits this band, as expected, into two components α_1 and α_1' (corresponding to the states of holes with the momentum projections $\pm 1/2$ and $\pm 3/2$). An unexpected feature is a strong nonlinear splitting of this line. When compression is applied along the [111] direction, we can see from Fig. 4 that the α_1 band is practically unsplit right up to $P = 30$ MPa. However, more precise experiments in which a study is made of the splitting of this band in the luminescence spectra by an interference method, demonstrated that the absence of splitting of α_1 in Fig. 4 is apparent. In fact, it follows from Ref. 5 that the absence of splitting is due to a change in the sign of the splitting on increase in the pressure. When the pressure is increased, the band α_1 first splits into two components, α_1 and α_1', which at $P = 22$ MPa merge again into one unpolarized band that splits into two components at still higher pressures P. It follows from Fig. 5 that at low pressures, when perturbation theory is valid, the deformation potential constant d' is small and positive, i.e., its sign is opposite to the sign of the band constant d. At high pressures the sign of the splitting of the α_1 band coincides with the band sign. If $d'/d < 0$, it follows that the expansion of the wave function of ED in terms of spherical vectors includes a considerable contribution from the vectors with $L = 2$ (Ref. 20).

We shall now consider the characteristics of the splitting of the band δ_1 (see the optical transition scheme in Fig. 4b). At pressures $P = 0$ and $\mathbf{P}\|[001]$ this band is missing from the photoconductivity spectrum. This is due to the strong forbiddeness of the $\{\Gamma_1\} \rightarrow \{\Gamma_1, \Gamma_5; \Gamma_8\}$ optical dipole transition, which creates a bound exciton in an excited state.[1] If the direction of pressure is $\mathbf{P}\|[111]$, mixing of the Γ_1 and Γ_5 states takes place[21] and the $\{\Gamma_1\} \rightarrow \{\Gamma_1, \Gamma_5; \Gamma_8\}$ transition becomes allowed, so that the photoconductivity spectra (Fig. 3) now include the bands and δ_1 δ_1'. As expected, at high pressures the polarization and the splitting of the δ_1 and δ_1' bands are the same as for the α_1 and α_1' bands. At low pressures the splitting of the δ_1 band is considerably greater than that of the α_1 band. This can be explained by assuming that the constant d' (naturally, we can speak of d' only in the range $P < 20$ MPa) depends on the state of ED and it is less for the $\{\Gamma_1, \Gamma_5; \Gamma_8\}$ state.

Equally surprising is the pressure dependence of the band α_1 when samples are compressed along the [001] direction. Splitting of the ED states in the $\mathbf{P}\|[001]$ case is small and is described by the deformation potential constant b'. We can see from Fig. 4 that in this case the sign of b' is identical with the sign of the band constant b. Nevertheless, the splitting depends nonlinearly on the applied pressure even when this pressure is low. As the pressure is increased, the amplitude of the α_1' band (hole momentum $\pm 3/2$, symmetry Γ_4) begins to decrease strongly at $P \approx 20$ MPa. However, the amplitude of the nearby band ω_1, which at $P = 0$ is characterized by a very small oscillator strength,[3)] begins to rise and at $P \approx 30$ MPa becomes comparable with the amplitude of the α_1 band. This can easily be explained by assuming that the ω_1 band in the photoconductivity spectrum is due to resonant photoexcitation of ED in a "hole" excited state of the Γ_8 symmetry. The interaction of this state with the Γ_6 state, corresponding to the band α_1' (if $\mathbf{P}\|[001]$), this state originates from the $\Gamma_8 = \Gamma_6 + \Gamma_7$ state), results in a nonlinear shift of these ED terms and an interchange of the oscillator strengths.

This model accounts satisfactorily also for the presence of a weak band (not labeled) near the α' line in Fig. 3b which exhibits a dependence of the spectral position on the pressure $\mathbf{P}\|[111]$ well illustrated in Fig. 4b. In this case a reduction of the symmetry from T_d to C_{3v} shifts the excited state Γ_8 to $(\Gamma_5 + \Gamma_6) + \Gamma_4$ and the ground state to $\Gamma_8 = (\Gamma_5 + \Gamma_6) + \Gamma_4$. Compression brings closer the terms Γ_4 and $\Gamma_5 + \Gamma_6$. However, in contrast to the preceding case the Γ_4 and $\Gamma_5 + \Gamma_6$ states should not interact strongly and, consequently, the corresponding oscillator strengths should not change.

An excited level (Fig. 4) discovered in this way had not been recorded earlier in the luminescence spectra. This had been due to two reasons: firstly, at liquid helium temperatures this level is weakly populated, and secondly, the corresponding oscillator strength is low. Nevertheless, it can be observed also in the luminescence spectra. All that is needed is to increase the temperature of a sample and to compress it along the [001] direction and thus increase its oscillator strength. A spectrum recorded under these conditions is shown as an inset in Fig. 3a. We can see that this luminescence spectrum shows clearly all three lines: $\alpha_1 \alpha_1', \omega_1$.

We shall consider in detail the transient excited states of ED, which are represented in the photoconductivity spectrum at $P = 0$ by the peaks labeled θ_1, ν_1, and $\varkappa_1$. The energy of ED in these states is considerably higher than the energy of a free exciton and, consequently, an ED complex in such a state should split (for energy reasons) into a neutral donor and a free exciton. However, if the symmetry of the excited state differs greatly from the symmetry of the ground state of a free exciton, such dissociation is hindered and the lifetime of an excited ED state may be quite long. We can see from Fig. 3 that all three peaks are considerably broadened, have low amplitudes, and are located in a wide photoconductivity "shoulder" which appears because of photoinduced creation of the D^- centers in a crystal. All this makes it difficult to study the corresponding excited states of ED. The width of the θ_1 and ν_1 peaks is independent of temperature and can be explained by the short lifetimes of the corresponding excited states ($\sim 10^{-11}$ s) in the case of ED $\rightarrow$ (D + free exciton) decay or in the case of the transition of ED to the ground state. Unfortunately, very little can be said about the nature of these excited states. If we assume that they are of the hole type, they should have the Γ_8 symmetry, because the θ_1 and ν_1 bands split into doublets when samples are compressed along the [001] direction (Fig. 4a).

On the basis of the above results we can expect a strong corrugation of the valence band and a complex system of excited states to be manifested in studies of the interaction of ED with a static magnetic field. We investigated the Zeeman luminescence spectra of bound excitons in germanium crystals compressed along the [001] and [111] directions. A magnetic field was directed along the compression axis. An analysis was made of the luminescence emerging at right-angles to this axis.

The interaction of a Γ_8 hole with a weak magnetic field or with a deformation field can be described by an interaction matrix deduced by the method of invariants.[23] When **B** and **P** are parallel to [001] or [111], the eigenvalues of this matrix, governing the splitting of the hole Γ_8 term, are given by

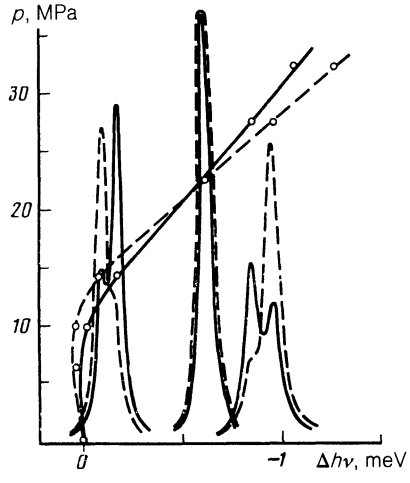

FIG. 5. Dependences of the spectral positions of the luminescence bands α_1 and α_1' of ED on the pressure applied along the [111] axis to a germanium crystal doped with phosphorus in a concentration of 3.5×10^{14} cm^{-3}. The dashed curves represent the luminescence polarized parallel to the deformation axis (α_1') and the continuous curves show the luminescence polarized perpendicular to this axis (α_1'). The figure includes also the luminescence spectra used in plotting the dependences.

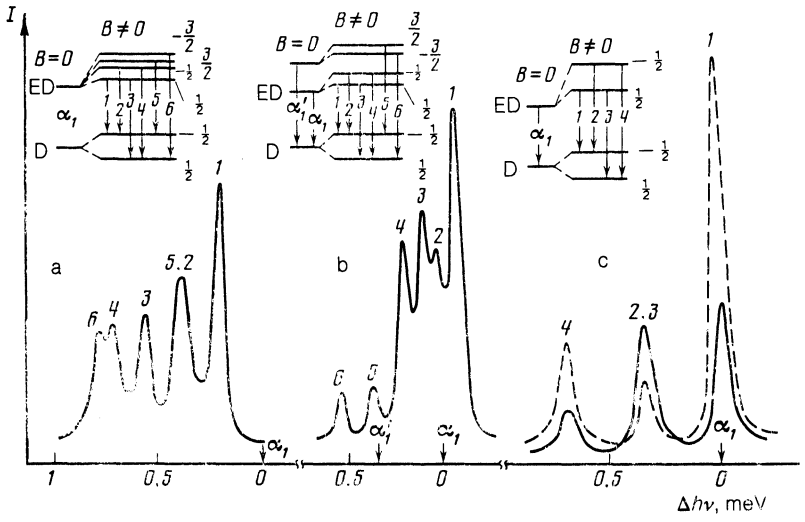

FIG. 6. Zeeman splitting of the zero-phonon α_1 luminescence bands of excitons bound to phosphorus atoms in germanium. Phosphorus concentration 3.5×10^{14} cm^{-3}, Voigt configuration (**B**||[001]), **P**||[001], $T=2$ K. The arrows give the spectral positions of the bands α_1 and α_1' obtained for $B=0$ and the position of the α_1 band is taken as 0. The insets show the optical transition schemes: a) $P=0$, $B=3.93$ T; b) $P=7.5$ MPa, $B=1.8$ T; c) $P=83.5$ MPa, $B=3.8$ T. The dashed curve is the luminescence spectrum polarized along the [001] axis and the continuous curve is the luminescence spectrum polarized at right-angles to the [001] axis.

$$E_{\pm k}=\pm k\mu_0 g_k^{\parallel}B+\lambda_k B^2+p_k, \qquad (2)$$

where in the case of compression along the [001] axis, we have

$$g_{1/2}^{\parallel}=(g_1+{}^1/_4 g_2),\ g_{3/2}^{\parallel}=(g_1+{}^9/_4 g_2),$$
$$\lambda_{1/2}=\lambda_1-\lambda_2,\quad \lambda_{3/2}=\lambda_1+\lambda_2,$$
$$p_{1/2}=-b'(S_{11}-S_{12})P,\quad p_{3/2}=b'(S_{11}-S_{12})P,$$

whereas for compression along the [111] axis, we obtain

$$g_{1/2}^{\parallel}=(g_1+{}^{13}/_4 g_2),\ g_{3/2}^{\parallel}={}^2/_3[({}^3/_2 g_1+{}^{23}/_8 g_2)^2+{}^1/_2 g_2^2]^{1/2},$$
$$\lambda_{1/2}=(\lambda_1-\lambda_2-\lambda_3/2),\quad \lambda_{3/2}=(\lambda_1+\lambda_2+\lambda_3/2),$$
$$p_{1/2}=-d'S_{44}P/\sqrt{3}=-p_{3/2},$$

where μ_0 is the Bohr magneton; S_{11}, S_{12}, and S_{44} are the elements of the S matrix; the constants g_k and λ_k represent the interaction of a Γ_8 hole with the applied magnetic field.

It follows from Eq. (2) that the Zeeman splitting of the hole levels with $j=\pm1/2$ and $j=\pm3/2$ is independent of P. We also note that in spite of the fact that Eq. (2) is valid at pressures such that the deformation splitting of the ED levels is small compared with the binding energy of an exciton, it can be used also at higher values of P if we assume that the parameters g_k and λ_k are functions of P.

We investigated the Zeeman splitting only of the zero-phonon α_1 band of the luminescence due to bound excitons. The Zeeman spectra obtained for different values of P are shown in Fig. 6. The optical decay schemes of ED plotted in Fig. 6 demonstrate that in the ground state there are two electrons that form a singlet state ($j=0$) of ED and do not contribute to the splitting of the ground state of ED. The dependences of the spectral positions of the Zeeman components on **B** labeled with numbers in Fig. 6, are plotted in Fig. 7. Figure 8 gives the pressure dependence of the $g_{1/2}^{\parallel}$ factor.

The range of the investigated pressures can be divided arbitrarily (Fig. 8) into three regions: in the first region ($0<P<10$ MPa) the parameters in Eq. (2) are practically unaffected, in the second region ($10<P<70$ MPa) there is a strong dependence of $g_{1/2}^{\parallel}$ on P, which changes to a weaker dependence in the third region ($P>70$ MPa). Throughout the investigated range of pressures the parameters $\lambda_{1/2}$ and $\lambda_{3/2}$ vary only slowly. A comparison of the experimental results with the calculations based on Eq. (2), carried out in the range $P<10$ MPa (i.e., where this equation is valid)

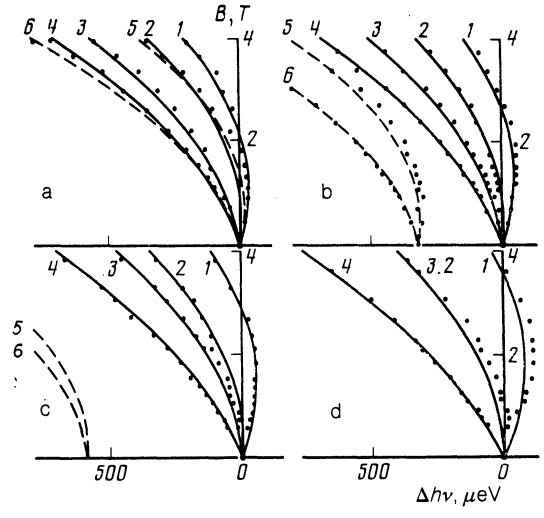

FIG. 7. Dependences of the spectral positions of the Zeeman components of the zero-phonon α_1 and α_1' luminescence bands of bound excitons on the magnetic field, recorded in the Voigt configuration (**B**||[001]). The concentration of phosphorus was 3.5×10^{14} cm^{-3}; **P**||[001], $T=2$ K. The points are the experimental results and the curves are calculated using equations given in the text (the dashed curves correspond to the hole momentum $\pm3/2$ and the continuous curves to $\pm1/2$). a) $P=0$; b) $P=7.5$ MPa; c) $P=20$ MPa; d) $P=83.5$ MPa.

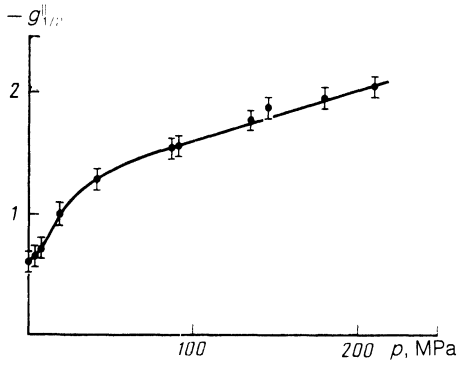

FIG. 8. Dependence of the $g_{1/2}^{\parallel}$ factor of a hole in ED on the pressure applied to a germanium crystal along [001]. Phosphorus concentration 3.5×10^{14} cm^{-3}, $T=2$ K.

enabled us to find the values of the constants[4)] occurring in Eq. (2):

$$g_1=-0.69, g_2=0.24,\ \lambda_1=0.33\ \mu\text{eV/kOe}^2,\ \lambda_2=0.036\ \mu\text{eV/kOe}^2,$$
$$\lambda_3=0.07\text{–}0.1\ \mu\text{eV/kOe}^2$$

The smallness of the g_1 and g_2 factors at low pressures P is due to nonanaliticity of the dispersion law of the valence band and a large contribution made to the wave function of ED by the spherical vectors with $L=2$. The strong dependence of the g factors on P at pressures 10–70 MPa may be attributed to the mixing of the ED states which occurs at these pressures (as pointed out above). This dependence is manifested in the spectra by a change in the number of peaks on increase in the pressure: instead of the four peaks at $P<70$ MPa, at pressures such that $g_h \approx g_e$, there are only three peaks in the spectrum (Fig. 6). It is interesting to note that the electron and hole g factors become equal when a sample is compressed along the [001] and [111] directions by approximately the same pressures. A weaker dependence observed at pressures $P>100$ MPa may be attributed to the mixing of the states with $j=\pm 1/2$ and $j=\pm 3/2$, which at low pressures are mixed only for small wave vectors **k**, i.e., in the region which makes only a small contribution to the wave function of ED. Clearly, the third region should begin with P such that the branches of the valence band intersect at points with $k\sim 1/a\approx 10^6\ \text{cm}^{-1}$ (a is the exciton radius), in agreement with the experimental results.

It follows from our experiments that the electron g factor ($g_e^{\parallel}$) of a sample compressed along the [001] direction is independent of pressure, whereas in the case of compression along [111] there is a change in accordance with the theory of Ref. 24. The values of $g^{\parallel}$ and $g^{\perp}$, which occur in the expression for $g_e^{\parallel}$, were determined by us from the splitting of the α_1 band when samples were compressed strongly along [001] and [111], and this gave the values of 0.91 and 1.92 for these factors. These values are in good agreement with those deduced from the ESR spectra in Ref. 25.

We regard it as our pleasant duty to thank Ya. E. Pokrovskiĭ and G. E. Pikus for their help in this investigation and for many valuable comments. We also thank V. A. Karasyuk and A. N. Safonov for discussing the results.

[1)] A complex consisting of k excitons bound to a neutral donor (D) will be denoted by $E_k D$.

[2)] The exchange interaction was ignored by us in an analysis of the recombination radiation (luminescence) spectra. Therefore, the Δ_i matrix dependent on 18 constants and describing this interaction is not given here. The Coulomb *e-h* interaction splits the $\{\Gamma_1, \Gamma_5; \Gamma_8\}$ state into four components ($\Gamma_5\times\Gamma_8\to\Gamma_6+\Gamma_7+2\Gamma_8$). If we allow for the exchange interaction, we find that this state should generally split into 25 states.

[3)] It is shown in Ref. 22 that optical transitions to closely spaced states of the same symmetry can have oscillator strengths differing by several orders of magnitude.

[4)] We determined these constants for excitons bound to arsenic atoms and found that $g_1=-0.68$, $g_2=0.28$, $\lambda_1=0.32$, and $\lambda_2=0.04$.

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