Crystal splitting of levels of exciton-impurity complexes in silicon

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A study was made of the spectra of the α_2 and α_3 luminescence bands of two- and three-exciton complexes bound to phosphorus atoms in silicon, subjected to magnetic fields of 20–50 kOe intensity applied along the [111] crystallographic axis, and also of the spectrum of the γ_1 band of bound excitons in an excited state P_1^*. The g factors of electrons and holes were not affected by an increase in the number of excitons bound to form many-particle exciton-impurity complexes. A comparison of calculations with the experimental results yielded the crystal splitting ($\Delta_{cr} = -0.16$ meV) of the state P_1^* and the spectrum of P_1^* was calculated in the absence of external perturbations.

Many-valley semiconductors with a degenerate valence band (Si and Ge) exhibit the so-called crystal splitting of the ground state of Wannier-Mott excitons, due to the anisotropy of the effective mass of electrons.[1] For example, an exciton in silicon may occupy two states with different absolute values with hole angular-momentum projection on the z axis, which is parallel to an electron valley. The energies of these states differ approximately by 0.3 meV (Ref. 2). The crystal splitting can be described approximately by including in the electron-hole interaction Hamiltonian a term of the type[3]

$$\mathcal{H}_{cr} = \frac{\Delta_{cr}}{2}\left(J_z^2 - \frac{5}{4}\right). \tag{1}$$

Here, J_z is the matrix of the projection operator of the angular momentum of a hole along the z axis and Δ_{cr} is the crystal splitting constant with the dimensions of energy.

There was a recent investigation[4] of electron-hole interaction in many-particle exciton-impurity complexes P_m formed at helium temperatures as a result of successive capture of several free excitons by neutral impurity atoms of phosphorus (P_0) in silicon. The complex P_m consists of m holes and $m+1$ electrons bound to a positively charged phosphorus ion. (Details of many-particle exciton-impurity complexes are given in Refs. 5 and 6.)

Many-particle exciton-impurity complexes are frequently described by a shell model[7] based on a one-electron approximation and on the hypothesis that the symmetry and multiplicity of degeneracy of one-particle states in these complexes are the same as for a neutral donor in the case of electrons and a neutral acceptor in the case of holes. The shells consist of one-electron states which have the same symmetry properties and the same energy and they are designated in the same way as the impurity-center irreducible symmetry-group T_d representations that govern the transformation of the one-particle wave functions.[8] Electrons first fill the symmetry state Γ_1 in which there can be two electrons with opposite spins, and then the states Γ_5 and Γ_3, which have a higher energy because of the orbit-valley splitting and which usually combine to form a shell $\Gamma_{3,5}$. In an exciton-impurity complex with $m \leqslant 4$ all the holes may be in the shell Γ_8 formed by a quartet of states which can be assigned approximately the angular momentum $j = 3/2$ and the projections of the momentum $m_j = \pm 3/2;\ \pm 1/2$.

Recombination of an electron and a hole may transform a complex P_m to P_{m-1} and this may be accompanied by the emission of a photon. Since silicon is an indirect-gap semiconductor, radiative recombination without phonon participation occurs mainly with electrons from the Γ_1 shell, because only these electrons interact sufficiently strongly with the central cell potential. The complex P_{m-1} is then created in an excited state P_{m-1}^* with a partly filled shell Γ_1. It was found in Refs. 9 and 10 that luminescence bands α_m corresponding to this process have a fine structure. Investigations of the fine structure of the zero-phonon luminescence line α_2 of two-exciton impurity complexes in uniaxially deformed crystals[4] have shown that this structure is mainly due to the interaction of the Γ_8 holes with an electron from the $\Gamma_{3,5}$ shell. It is assumed that at 2 K the electron is in the Γ_5 state.

The Hamiltonian of the interaction of an Γ_5 electron with a Γ_8 hole, constructed in Ref. 4 by the method of invariants[1] ignoring the intervalley scattering of an electron by the potential of its interaction with a hole, is of the form

$$\begin{aligned}\mathcal{H}^{eh} = {}& \Delta_0 + \Delta_1 \sum_i J_i\sigma_i + \Delta_2 \sum_i J_i^3\sigma_i \\ & + \Delta_3 \sum_i (L_i^2 - {}^2/_3) J_i\sigma_i + \Delta_4 \sum_i (L_i^2 - {}^2/_3) J_i^3\sigma_i \\ & + \Delta_5 \sum_{ijk} \varepsilon_{ijk} L_j^2 V_k\sigma_k + \Delta_6 \sum_i (L_i^2 - {}^2/_3) J_i^2, \quad i = x, y, z, \\ & V_i = \sum_{k_f} \frac{\varepsilon_{ijk}}{2} (J_iJ_j^2 + J_j^2J_i),\end{aligned} \tag{2}$$

where ϵ_{ijk} is the totally antisymmetric unit pseudotensor. Here, L_i, $\sigma_i/2$, and J_i are matrices of the angular momentum operator expressed in terms of the bases of the one-particle wave functions, and Δ_1–Δ_6 are phenomenological interaction constants with the dimensions of energy. The values of the constants Δ_1–Δ_5 representing the electron-hole exchange were determined from experimental investigations of the fine structure of the band α_2 when silicon was subjected to uniaxial compression and dilatation along the [001]

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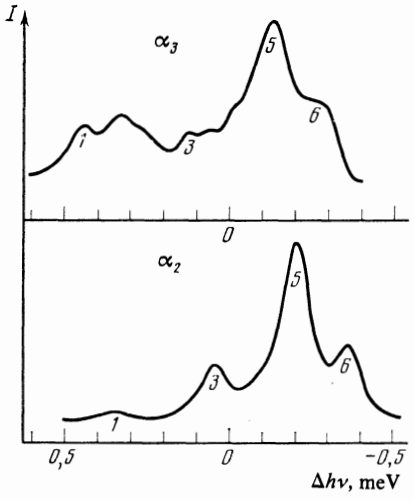

FIG. 1. Spectra of the α_2 and α_3 luminescence bands in a magnetic field $H = 33$ kOe, $\mathbf{H} \| [111]$, $T = 2$ K.

axis. This enabled us to calculate from Eq. (2) the fine structure of α_2 for other deformation directions ([111] and [110]) in satisfactory agreement with the experimental data. The value of the constant Δ_6 occurring in Eq. (2) next to the term allowing for the crystal splitting ($\Delta_6 = -\Delta_{cr}/2$) was indeterminate because uniaxial deformation lifted the spatial degeneracy of the hole states and the crystal splitting was not manifested in the fine structure. In the present study the crystal splitting constant Δ_6 was found from the experimental data on the Zeeman splitting of the α_2 band of an undeformed crystal, which made it possible to calculate and compare with experiment the fine structure of the levels of an excited state of a bound exciton P_1^* in the absence of external perturbations.

We studied the splitting of the zero-phonon luminescence lines α_2 and α_3 of many-particle exciton-impurity complexes, bound to phosphorus atoms in silicon subjected to a magnetic field of 20–50 kOe intensity oriented along the [111] axis, and also the fine structure of the luminescence band γ_1 (Ref. 9) corresponding to radiative decay of bound excitons P_1^* accompanied by a transition to the Γ_5 state of a neutral donor. A sample in the form of a Weierstrass sphere made of single-crystal silicon was grown by the zone melting method and doped with phosphorus in a concentration of 2×10^{14} cm^{-3}; it was placed in liquid helium and excited with argon laser radiation of $\sim$0.3 W power. A magnetic field was created by a superconducting solenoid. The recombination radiation (luminescence) spectra were recorded using an interference method described in Ref. 11, which ensured a high spectral resolution of the Zeeman components. The spectrum of the γ_1 band was recorded by placing a sample with a phosphorus concentration of 10^{15} cm^{-3} in liquid helium and subjecting it not only to excitation with laser radiation, but also to an alternating electric field of 68 MHz frequency and of intensity amounting to a few volts per centimeter.[4] This made it possible to increase significantly the concentration of bound excitons which were in the excited state P_1^*.

Figure 1 shows the Zeeman spectra of the α_2 and α_3 luminescence bands representing two- and three-exciton complexes, respectively. When the magnetic field intensity was $H > 30$ kOe, the paramagnetic splitting was greater than the splitting caused by the interaction between bound electrons and holes, so that we assumed approximately that each particle was in a state with a definite projection of the magnetic moment along the magnetic field direction. This made it possible to classify the optical transitions in various many-particle exciton-impurity complexes in accordance with the spin states of recombining electrons and holes (Fig. 2).

At 2 K the filling occurred mainly in the ground spin sublevel of a two-exciton complex P_2 with the projection of the total angular momentum of $M_J = -5/2$ along the field direction. Therefore, the spectrum of the α_2 band consisted of three main components[12,13] corresponding to transitions to the levels of the excited state P_1^* of a bound exciton with $M_J = -5/2$ and $M_J = -3/2$:

$$P_2\left\{\Gamma_1\left(-\frac{1}{2},+\frac{1}{2}\right)\Gamma_5\left(-\frac{1}{2}\right)\Gamma_8\left(-\frac{3}{2},-\frac{1}{2}\right)\right\} \rightarrow P_1^* \begin{cases} \{\Gamma_1(-1/2)\Gamma_5(-1/2)\Gamma_8(-3/2)\} & (3) \\ \{\Gamma_1(-1/2)\Gamma_5(-1/2)\Gamma_8(-1/2)\} & (5) \\ \{\Gamma_1(+1/2)\Gamma_5(-1/2)\Gamma_8(-3/2)\} & (6) \end{cases} \quad (3)$$

The curly brackets in the above expression contain the distribution of electrons and holes among the shells in the P_2 and P_1^* complexes, and the numbers in parentheses after the shell symbols denote the spin states of the particles that populate these shells. Under these conditions the α_3 band has a complex structure with more than six components, i.e., components are present corresponding to the recombination of particles which are in the same spin states, but differ in respect of the states of the particles that do not participate in the recombination process.

Figure 3 shows the dependences of the spectral positions of the Zeeman components of the α_2 band and of the corresponding component of the α_1 (Ref. 11) and α_3 bands on the magnetic field intensity H. In the range $H > 30$ kOe

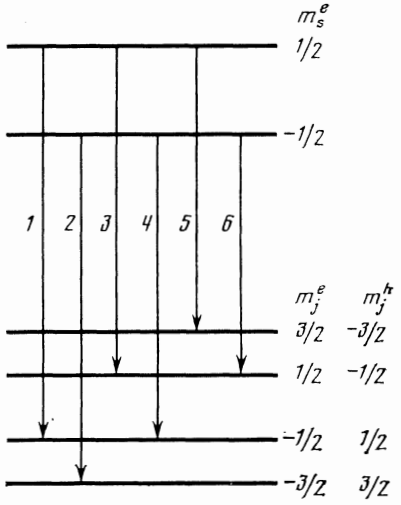

FIG. 2. Allowed optical transitions corresponding to the recombination of a Γ_1 electron with a Γ_8 hole; m_s^e and m_j^e are the projections of the angular momentum of an electron in the initial and final states; m_j^h is the projection of the angular momentum of a recombining hole.

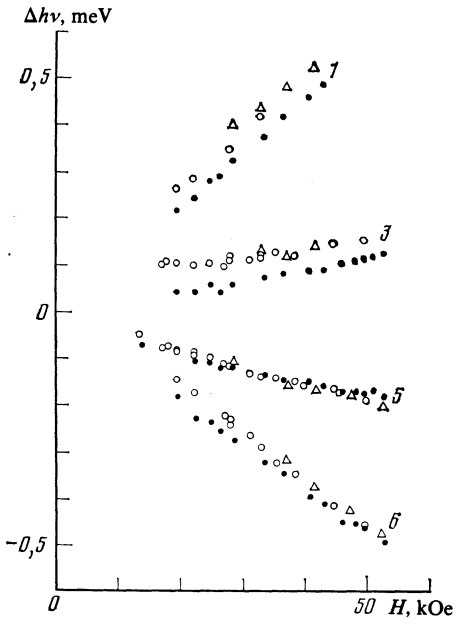

FIG. 3. Dependences of the spectral positions of the Zeeman components of the α_1 (●) band (Ref. 11), and of the α_2 (○) and α_3 (△) bands on the magnetic field H.

the slope of these dependences is practically independent of the luminescence band number, which shows that the g factors of electrons and holes are practically unaffected by an increase in the number of excitons bound to form an exciton-impurity complex. In the range of low values of H the Zeeman dependences of the bands α_2 and α_3 differ considerably from the corresponding dependences for the band α_1. These differences are due to the effects of the interaction between the bound charges, resulting in mixing of the "pure" states with specific projections of the angular momenta of individual particles along the magnetic field direction.

Since the initial state in transitions corresponding to the components 3, 5, and 6 of the α_2 band is the same, the splitting between these components represents directly the structure of the levels in the final state, which is an excited state

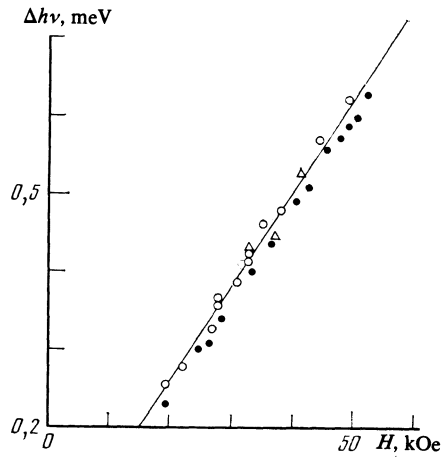

FIG. 4. Dependences of the splitting between the Zeeman components 3 and 6 of the α_1 (●), α_2 (○), and α_3 (△) bands on H.

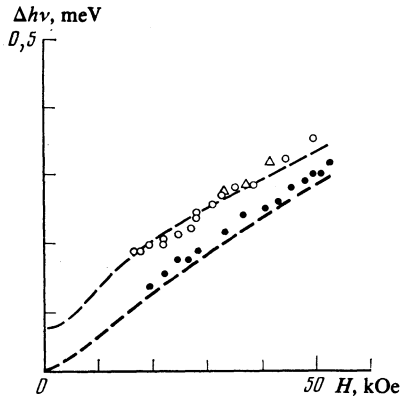

FIG. 5. Dependences of the splitting between the Zeeman components 3 and 5 of the α_1 (●), α_2 (○), and α_3 (△) bands on H. The upper curve is calculated for $\Delta_6 = 0.08$ meV and the lower curve for $\Delta_6 = 0$.

P_1^* of a bound exciton. The dependences of the splitting between these components on H are plotted in Figs. 4 and 5. The components 3 and 6 differ only in respect of the projection of the electron spin in the Γ_1 shell of the P_1^* complex. Since its exchange interaction with the hole and with the electron from the $\Gamma_{3,5}$ shell is slight,[4] the splitting between the components 3 and 6 is simply equal to the paramagnetic splitting of the states of the Γ_1 electron and, therefore, it is directly proportional to the magnetic field intensity. The slope of the corresponding dependence is governed by the g factor of the Γ_1 electron and it is practically identical with the slope of the analogous dependence in the case of the α_1 band. In the limit of high values of H the components 3 and 5 of the α_2 band differ only in the projection of the momentum of the hole in P_1^*. We can see from Fig. 5 that the field dependence of the splitting between these components differs considerably from the corresponding dependence in the case of the α_1 band, owing to the interaction of a hole with an electron from the $\Gamma_{3,5}$ shell.

Just as in Ref. 4, we shall ignore the populations of the electron states Γ_3 and the intervalley scattering of an electron on the potential of its interaction with a hole. In this case the electron-hole interaction is described by the Hamiltonian (2). We shall add to it the Hamiltonian of the interaction with the magnetic field[14]

$$\mathcal{H}(\mathbf{H}) = \mu_B \left(\frac{g^e}{2} \sum_i \sigma_i H_i + g_1^h \sum_i J_i H_i + g_2^h \sum_i J_i^3 H_i \right) + (q^e + q_1^h) H^2 + q_2^h \left(\sum_i J_i H_i \right)^2 + q_3^h \sum_i J_i^2 H_i^2 \quad (4)$$

(here, μ_B is the Bohr magneton; g^e, g_1^h, and g_2^h are the g factors; q^e, q_1^h, q_2^h, and q_3^h are the constants of the quadratic shift of the one-particle states) and solve the secular equation $\mathcal{H}^{eh} + \mathcal{H}(\mathbf{H}) - \lambda] = 0$ so as to calculate the dependence of the splitting between the levels of P_1^* on the magnetic field. The results of such a calculation of the difference between the energies of the components 3 and 5 of the band α_2 are represented by the upper curve in Fig. 5; the g factors and the quadratic shift constants were assumed to be the same as for the α_1 band (Ref. 11). {If $H \| [111]$, of all the

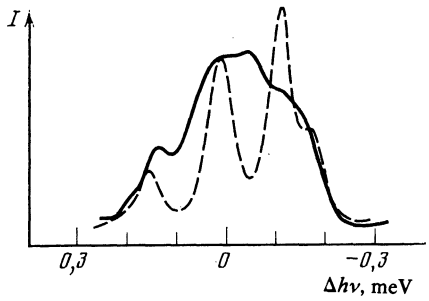

FIG. 6. Experimental (continuous curve) and theoretical (dashed curve) spectra of the γ_1 band.

quadratic terms only that in front of q_2 contributes to the splitting and its value is $q_2 = (b_{3/2} - b_{1/2})/2 = 1 \times 10^{-5}$ meV/kOe^2.} The values of the constants Δ_1–Δ_5 were assumed to be the same as in Ref. 4. The constant $\Delta_6 = 0.08$ meV was selected to achieve the best agreement with the experimental results. The lower curve in Fig. 5 gives the calculations carried out for $\Delta_6 = 0$. We can see that the calculated dependence is quite sensitive to the value of the constant Δ_6. Therefore, the crystal splitting representing the interaction of a Γ_8 hole with a Γ_5 electron in exciton-impurity complexes bound to phosphorous atoms in silicon amounts to $\Delta_{cr} = -2\Delta_6 \approx -0.16$ meV.

Using the above value of the constant Δ_6, we were able to calculate from Eq. (2) the spectrum of P_1^* in the absence of external perturbations but allowing for the crystal splitting. The results of this calculation are presented in Fig. 6, where the dashed curve is the theoretical spectrum of the γ_1 band corresponding to the following system of the P_1^* levels (meV): 0.191; 0.055; 0.055; 0.037; −0.068; −0.069; −0.069; −0.132. The continuous curve in this figure is the spectrum of the γ_1 band obtained by averaging of three experimental spectra. We can see that the scales of splitting are the same in the calculated and experimental spectra, although the lattice spectrum has a more complex structure. If we ignore the crystal splitting, then the scale of the splitting in the calculated spectrum is halved. This discrepancy between the theory and experiment may be due to inaccurate determination of the constants Δ_1–Δ_6 or due to inaccuracy of our assumptions. Moreover, the components of the γ_1 band may be broadened because of the finite lifetime of the Γ_5 state of a neutral phosphorous donor.[13] The reason why the γ_1 band is even slightly wider than the α_2 band (Refs. 13 and 4) for which P_1^* is the final state is (as indicated by rough calculations) that the components at the edges of the α_2 band have a very low intensity because of the smallness of the oscillator strengths for optical transitions from the lower levels of P_2 to the upper levels of P_1^* and from the upper levels of P_2 to the lower levels of P_1^*.

Our investigation thus demonstrates that the Zeeman effect in many-particle exciton-impurity complexes can be described using the shell model as the zeroth approximation and allowing for the interaction between bound carriers regarded as a small perturbation. We can then assume that the g factors of the one-particle states are independent of the number of excitons bound in such complexes. A comparison of the experimental and theoretical dependences of the splitting between the Zeeman components of the α_2 band on the magnetic field intensity and a study of the fine structure spectra of the γ_1 band demonstrate the need to allow for the crystal splitting in calculating the fine structure of levels of exciton-impurity complexes, which in the case of an excited state of a bound exciton P_1^* amounts to $\Delta_{cr} = -0.16$ meV.

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