

¹⁾We use the atomic system of units $\hbar = e = m = 1$.

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Luminescence of excitons bound to phosphorus atoms in silicon subjected to a magnetic field

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An investigation was made of the luminescence spectra of excitons bound to phosphorus atoms in silicon. A magnetic field of 18-55 kOe intensity directed along the [001] and [111] crystallographic axes was applied to the samples in the Faraday and Voigt configurations. The values of the electron ($g_e = 2.0$) and hole ($g_h = 0.83$, $g_2 = 0.22$) g factors and the diamagnetic shifts were determined; these were found to depend on the initial state of holes in bound excitons. The amplitudes of the Zeeman components in these spectra were in satisfactory agreement with the calculations carried out using the shell model approximation for bound excitons.

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1. INTRODUCTION

Recent progress in the understanding of the structure of many-particle exciton-impurity (EI) complexes¹ has largely been due to the application of the shell model proposed in Refs. 2 and 3. In particular, this model has made it possible to interpret satisfactorily the main features of the luminescence spectra of EI complexes in silicon subjected to magnetic fields.^{4,5} However, we must bear in mind that the luminescence bands of EI complexes formed as a result of binding m excitons to neutral group III or V atoms in silicon have a fine structure if $m > 1$ even if there are no external perturbations.⁶ Separations between the individual components of a luminescence band can reach 200 μ eV, i.e., they are comparable with the separations between the Zeeman

components in magnetic fields $H \lesssim 50$ kOe. The Zeeman spectra of EI complexes can be interpreted simply if we know exactly the constants (in particular, the electron and hole g factors) representing the initial and final states of bound carriers in magnetic fields.

We must bear in mind that, in the case of EI complexes bound to donors in silicon, the α -series luminescence lines^{2,3} appear on recombination of electrons from the state Γ_1 in which there cannot be more than two electrons and which is filled even for a bound exciton if $m = 1$. We shall assume that the necessary constants can be determined sufficiently accurately by analyzing the Zeeman spectra of excitons bound to neutral donors in silicon (i.e., by analysing the spectra of EI complexes with $m = 1$), which can then be used to

interpret the splitting of the α -series lines of larger EI complexes.

However, the published experimental data are still insufficient for determining reliably the g factors and diamagnetic shifts when excitons are bound to donors in silicon. For example, Cherlow *et al.*⁷ investigated the Zeeman spectra of excitons bound to arsenic atoms; this was done at 4.2 °K in magnetic fields of 60–90 kOe. Under these conditions only the lowest state of a bound electron is fairly strongly populated and the intensities of the lines corresponding to the recombination of holes from excited states are low. Bearing in mind that Cherlow *et al.*⁷ used apparatus with a relatively low resolution, one is forced to the conclusion that the spectral positions of some of the Zeeman components are not yet known reliably. Moreover, in the investigated range of magnetic field intensities the linear and quadratic terms of the line shifts make comparable contributions and, therefore, it is difficult to determine the g factors and diamagnetic shifts. Kulakovskii *et al.*⁵ determined these constants from a set of Zeeman spectra of EI complexes containing phosphorus atoms ($m = 1, 2, 3, 4$). The values obtained in Ref. 5 were very different from those reported in Ref. 7.

We carried out a detailed investigation of the Zeeman spectra of excitons bound to phosphorus atoms in silicon subjected to magnetic fields $H = 18$ –55 kOe; the measurements were made using high-resolution interference spectroscopy and the electron and hole g factors as well as the constants representing diamagnetic shifts were determined. Moreover, the amplitudes of the various Zeeman components were compared with the calculations carried out using the shell model of bound excitons.

2. EXPERIMENTAL METHOD

The resolving power of the spectroscopic system was improved by passing this radiation through a high-luminosity MDR-2M monochromator and then applying an additional analysis with a Fabry-Perot interferometer. The interferometer was a Fabry-Perot etalon of the IT-51-30 type with a fixed distance between the mirrors h ; it was placed inside a chamber with a gas whose pressure could be varied slowly between -1 and $+1.5$ atm by admitting or evacuating the gas via needle valves. In this way the path difference between the interfering beams was altered and the spectrum was scanned. Multilayer dielectric-coated mirrors, ensuring a reflection coefficient of about 85% in the 1 – 1.1μ range, were used in the interferometer. The resolution was at least $40 \mu\text{eV}$ for $h = 1$ mm and $60 \mu\text{eV}$ for $h = 0.6$ mm. The working gas was usually Freon-13, which was transparent in the range of wavelengths of interest to us and had a relatively high refractive index sufficient for scanning the spectrum within two interference orders. A pointer manometer was used as the pressure gauge; a thin-walled metal can with a wedge-shaped cut along its generator, which rotated together with the pointer, was attached to the axis of the gauge. A small incandescent lamp was placed inside the can and the radiation of this lamp passed through the

wedge-shaped cut and reached a slit behind which there was a photodiode. The system was tuned so that the voltage across the load resistor of the photodiode was proportional to the width of the wedge-shaped cut and, consequently, to the angle of rotation of the pointer and the pressure in the interferometer chamber. This voltage was applied to the X input of an X - Y plotter and ensured linear scanning of the spectrum. The interference pattern was focused in the plane of an iris diaphragm selecting the central zone. Behind the diaphragm there was an FÉU-62 photomultiplier cooled with liquid nitrogen. Cooling reduced by about three orders of magnitude the dark current of the photomultiplier so that under the experimental conditions employed it was less than one pulse/sec. Current pulses from the photomultiplier were amplified first before reaching a unit which measured the counting rate (UIM-2-1eM), in which automatic switching of the ranges was replaced with manual operation and additional integrating circuits were introduced. The voltage from the measuring unit output reached the Y input of the plotter. The tuning and absolute calibration of the interferometer were made using a helium-laser emitting at 1.15μ .

Phosphorus-doped silicon samples were investigated. The phosphorus atoms formed "ideal" donor centers at the crystal lattice sites because the atomic number of phosphorus exceeds by unity the atomic number of silicon. However, these investigations showed that the method of doping with phosphorus had a considerable influence on the EI luminescence. For example, in the case of the samples doped with phosphorus during growth of single crystals there was a considerable broadening of the no-phonon (NP) luminescence line of bound excitons. The samples were doped with phosphorus by irradiation of pure silicon single crystals with slow neutrons ($\text{Si}^{30} + n_0 \rightarrow \text{Si}^{31} + \beta^-$) and there was no significant broadening of this line. When the spectra were recorded, the width of the NP line did not exceed $45 \mu\text{eV}$ (Fig. 1); this was slightly greater than the instrumental width and lower than that reported in Ref. 6. Therefore, we subsequently studied only the samples of the "neutron"-doped silicon with a phosphorus concentration of $2 \times 10^{14} \text{ cm}^{-3}$ containing small amounts of boron as a residual impurity. Samples were cut approximately into prisms, each of whose faces was oriented at an angle of 45° relative to the axis of the sample and played the role of a dielectric mirror (inset in Fig. 1); next, the samples were mechanically polished and placed in a helium bath of a metal cryostat inside the superconducting solenoid channel. The samples were excited by radiation from an argon laser of up to 0.5 W power; this radiation was focused in the form of spots of about 50μ size on those parts of the surface which were previously etched in CP-4A to reduce the surface recombination velocity. The recombination radiation emitted either along the magnetic field ($S \parallel H$, Faraday configuration) or at right-angles to the magnetic field ($S \perp H$, Voigt configuration) and reflected from a dielectric mirror at the sample was projected onto the monochromator slit. The relevant beams were selected by placing under the

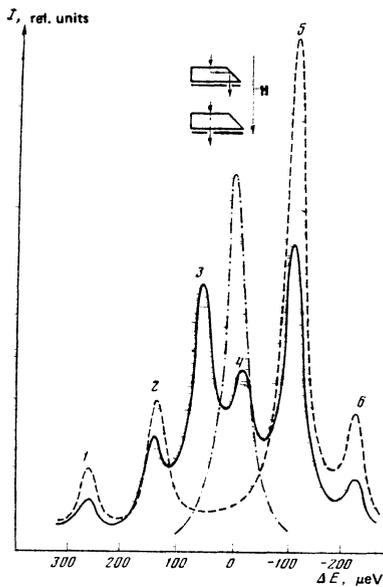


FIG. 1. No-phonon (NP) component of the luminescence due to excitons bound to phosphorus atoms in silicon at 4.2°K. The chain curve is obtained in the absence of a magnetic field ($H = 0$); the continuous curve is the spectrum recorded in $H = 23.3$ kOe, $H \parallel [111]$, $S \perp H$; the dashed curve is the spectrum recorded in $H = 23.3$ kOe, $H \parallel [111]$, $S \parallel H$.

sample a metal mask with windows for the extraction of the luminescence in one of these configurations. In the absence of a mask, the spectral system contained the radiation emitted in various directions, which distorted the amplitude relationships between the peaks in the Zeeman spectra. In some cases an increase in the radiation flux and an improvement in the precision of determination of the Zeeman splitting were achieved by using a sample in the form of a Weierstrass sphere 10 mm in diameter, whose axis was oriented in the $[111]$ direction parallel to the magnetic field.

The pulse counting rate at the peaks of the Zeeman components amounted to hundreds of pulses per second, i.e., it was much higher than the counting rate in darkness. The shot noise during counting was reduced by integrating the output signal. As a result of this procedure the noise component did not exceed 3% of the maximum value of the signal.

Linear polarization of the luminescence was investigated by placing, behind the exit window of the cryostat, a film polarizer whose axis could be rotated so that it passed radiation polarized either parallel or perpendicular to the magnetic field. The influence of the instrumental polarization was eliminated by altering the gain of an automatic plotter which was selected so that when the polarizer was rotated in the absence of the magnetic field the intensity of the bound-exciton luminescence line was unaffected. Total polarization of the Zeeman components was expected in the Voigt configuration. However, the experimental results showed that the degree of polarization was about 30%. The strong depolarization was clearly due to the complex geometry used to deflect the luminescence along the direction perpendicular to the magnetic field. Nevertheless, the sum of the spectral curves recorded

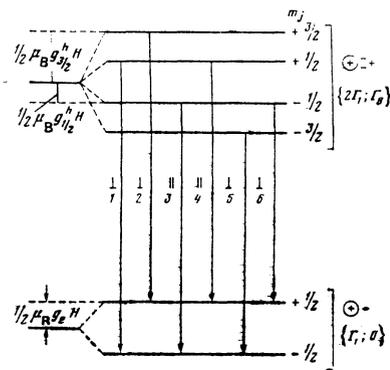


FIG. 2. Splitting scheme for the states of an exciton bound to a donor in silicon and for the states of a neutral donor in a magnetic field. The symbols \parallel and \perp correspond to the luminescence parallel and perpendicular to the magnetic field.

for the two polarization directions gave the luminescence spectrum which could be compared correctly with the results of calculations because in this case the influence of the luminescence polarization on the transmission by the spectroscopic apparatus was compensated.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the no-phonon (NP) spectra of the luminescence due to excitons bound to phosphorus atoms in silicon, recorded in the absence and presence of a magnetic field at 4.2°K. It is clear from Fig. 1 that if $S \parallel H$, the luminescence line splits into four components, whereas for $S \perp H$ it splits into six components. This nature of splitting follows from the scheme of Ref. 8 shown in Fig. 2. The initial state of the system is a bound exciton, consisting of a singly charged positive impurity ion, two electrons, and a hole; the final state is a neutral donor containing an impurity ion and an electron. In the initial state $\{2\Gamma_1; \Gamma_8\}$ (Refs. 3 and 8) the two electrons have spins directed in opposite ways and they fill the Γ_1 shell. Therefore, the magnetic field does not split the electron states but it does split the Γ_8 hole state with a total angular momentum of $3/2$ into four terms with the $\pm 3/2$ and $\pm 1/2$ projections of the angular momentum along the magnetic field. In the final state $\{1\Gamma_1; 0\}$ there is one electron whose angular momentum has a projection $\pm 1/2$ along the magnetic field. The "allowed" optical transitions are those for which the projection of the total angular momentum of the system along the magnetic field changes by ± 1 or remains unaltered. In the latter case there is no luminescence parallel to the magnetic field. When these selection rules are applied, we can see that in the $S \parallel H$ case we should observe the Zeeman components denoted in Figs. 1 and 2 by 1, 2, 5, and 6, whereas in the $S \perp H$ case all six radiative transitions should be observed. At lower temperatures the amplitudes of the Zeeman components, except for peak 5, decrease considerably (this applies particularly to peak 2), supporting the proposed identification.

In reality, the wave functions corresponding to the terms in Fig. 2 are not generally speaking the eigenfunctions of the operator of the projection of the angular

momentum of a hole \mathbf{J} onto the magnetic field direction. According to the shell model the Zeeman splitting for holes is governed, as in the case of a neutral acceptor, by the perturbation matrix which can be written in the following form on the basis of the symmetry considerations⁹:

$$\mathcal{H}_h = \mu_B (g_1 \mathbf{JH} + g_2 \sum_i J_i^2 H_i), \quad (1)$$

where μ_B is the Bohr magneton, g_1 is the isotropic contribution, and g_2 is the anisotropic correction. For $g_2 = 0$, we have $g_{1/2}^h = g_{3/2}^h$ and these contributions are independent of the magnetic field direction. The angular dependence of the wave function of a hole at an impurity center in silicon may result in nonzero values of g_2 and, therefore, the Zeeman splitting may depend on the magnetic field orientation. Solution of Eq. (1) for $g_1 = 0.8$ and $g_2 = 0.2$ (close to the experimental values for bound excitons reported below) shows that in this case the eigenfunctions are practically identical with the eigenfunctions of the projection of the operator \mathbf{J} onto \mathbf{H} . Therefore, the use of the projections of the hole angular momentum $\pm 1/2$ and $\pm 3/2$ represents a satisfactory approximation. These calculations also show that the probability of "forbidden" transitions not shown in Fig. 2 is several orders of magnitude greater than the probability of "allowed" transitions although the hole states are "mixed."

It follows from the above discussion that the g factors of holes can be represented in the following form⁹: if $\mathbf{H} \parallel [001]$, then

$$g_{1/2}^h = g_1 + 1/4 g_2, \quad g_{3/2}^h = g_1 + 3/4 g_2; \quad (2)$$

in the case when $\mathbf{H} \perp [111]$, we have

$$g_{1/2}^h = g_1 + 1/4 g_2, \quad g_{3/2}^h = 1/3 [6(g_1 + 3/4 g_2)^2 + 3(g_1 + 1/4 g_2)^2]^{1/2}. \quad (3)$$

The final state of the transition is governed by the projection of the electron spin $\pm 1/2$ in the neutral-donor shell Γ_1 and has the same g factor as the electron value g_e .

The initial and final energies should contain not only linear terms but one which is quadratic in H and associated with the diamagnetic susceptibility of EI complexes:

$$\Delta E = bH^2, \quad (4)$$

where b depends on the spatial localization of the wave functions and on the effective masses.^{5,10}

Figure 3 shows the dependences of the shifts of the Zeeman components on the magnetic field H applied along two crystallographic directions: $\mathbf{H} \parallel [001]$ and $\mathbf{H} \parallel [111]$. A least-squares analysis of the results in Fig. 3 gives the values of the g factors and of the coefficients b representing the diamagnetic shift. These values are listed in Table I together with the quantities defined in Refs. 5 and 7. The precision of the estimates of the g factors given here is estimated to be ± 0.05 . Within the limits of this precision the experimental results of Fig. 3 can be described well by the constants listed in Table I. The precision of determination of the coefficients b in the quadratic term of the Zeeman splitting in Eq. (4) is considerably less because

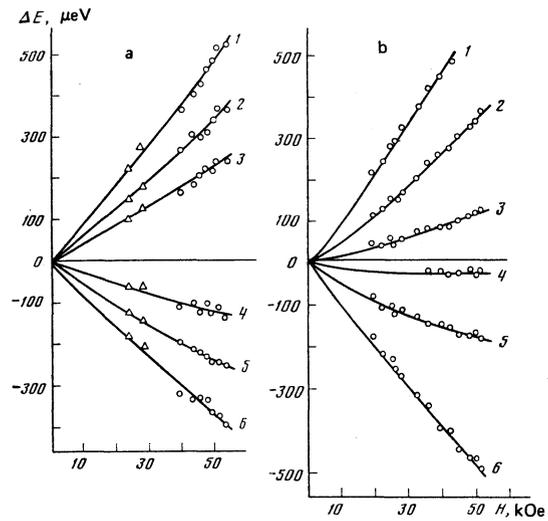


FIG. 3. Spectral shifts ΔE of the Zeeman components of the NP luminescence line of excitons bound to phosphorus atoms in silicon plotted as a function of the magnetic field H : a) $\mathbf{H} \parallel [001]$; b) $\mathbf{H} \parallel [111]$. The continuous curves are plotted on the basis of Eqs. (1)–(4) using constants listed in Table I. The symbols \circ ($h = 0.6$ mm) and Δ ($h = 1$ mm) are the experimental values.

of weak magnetic fields used in the measurements and it is estimated to be ± 0.5 . It is clear from Table I that our value of g_e is somewhat higher than those given in Refs. 5 and 7, but it agrees with the value of g_e obtained for an electron localized at a simple donor in silicon.¹¹ The values of g_1 and g_2 are in satisfactory agreement (although they are not identical) with those determined in Ref. 7, but they are quite different from the values given in Ref. 5. It should be stressed that in Ref. 7 and in the present study the g factors are found for excitons bound to different group V impurities in silicon: arsenic and phosphorus. A satisfactory agreement between the g factors shows that the chemical nature of the donor atom to which an exciton is bound does not play a decisive role in the interaction of EI complexes with the applied magnetic field. A considerable discrepancy between our results and those in Ref. 5 can be explained by the fact that the splitting of the EI spectra with $m = 2$ or 3 in the absence of perturbations is comparable with the Zeeman splitting and, therefore, determination of the g factor from the Zeeman spectra of EI complexes with different values of m , used in Ref. 5, can hardly be regarded as accurate. It is also clear from Table I that, in spite of the high precision of the determination of the constants b , the

TABLE I.

Crystallographic direction	Source	g_e	$g_{1/2}^h$	$g_{3/2}^h$	g_1	g_2	$b_{1/2} \cdot 10^4, \mu\text{eV/kOe}^2$	$b_{3/2} \cdot 10^4, \mu\text{eV/kOe}^2$
(001)	our results	2.04	0.86	1.33	0.80	0.24	1.6	2.1
	[7]	1.85	0.79	1.24	0.74	0.22	1.85	1.85
(111)	our results	1.99	1.54	1.27	0.86	0.21	1.5	3.4
	[7]	1.85	1.46	1.17	0.74	0.22	1.85	1.85
	[5]	1.9	1.8	1.2	0.6	0.4	2.2	2.2

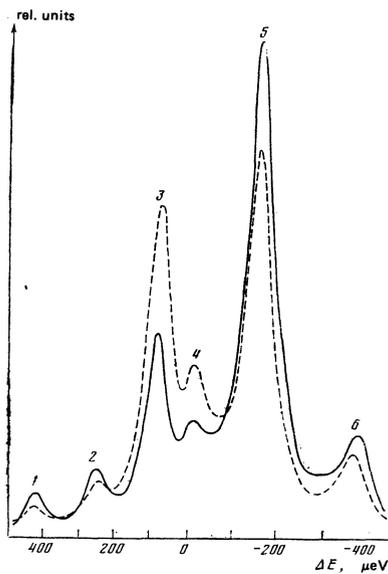


FIG. 4. Zeeman spectrum of the NP line of the luminescence due to excitons bound to phosphorus atoms in silicon, recorded at 4.2°K for two directions of polarization in a magnetic field $H = 38$ kOe, $H \parallel [111]$. The continuous curve corresponds to $e \perp H$ and the dashed curve to $e \parallel H$.

difference between the diamagnetic shifts for the hole states $\pm 1/2$ and $\pm 3/2$ exceeds a possible error. This is not surprising because the spatial localization of the wave functions of holes differ considerably from one state to another.

We shall conclude by considering the amplitude relationships between various Zeeman components of the spectra. Figure 4 shows one of the spectra recorded for two directions of polarization of the bound-exciton luminescence ($e \parallel H$ and $e \perp H$, where e is the electric field vector of the luminescence). Summation of these two spectra eliminates the influence of the difference between the transmission of the apparatus for luminescence with different polarizations. The experimental values of the relative intensities obtained in this way are listed in Table II. This table includes also the relative probabilities of radiative transitions for the Zeeman components calculated in Ref. 3 without allowance for the populations of the initial hole states of bound excitons ($T = \infty$), as well as calculated intensities of the luminescence for the populations corresponding to $T = 4.2^\circ\text{K}$ and the splitting of the initial states given in Fig. 4. Bearing in mind that some of the relatively weak peaks (for example those denoted by 2 and 4) recorded in the experimental spectra are located at

TABLE II.

Transitions	Relative intensity			Transitions	Relative intensity		
	calc, $T = \infty$	calc $T = 4.2^\circ\text{K}$, $H = 38$ kOe	exper.		calc., $T = \infty$	calc. $T = 4.2^\circ\text{K}$, $H = 38$ kOe	exper.
1	1/3	0.07	0.06	4	4/3	0.28	0.31
2	1	0.10	0.12	5	1	1	1
3	4/3	0.72	0.59	6	1/3	0.18	0.18

shoulders of stronger peaks, so that the precision of the determination of the relative intensities is low, we may conclude from Table II that the experimental results agree well with the calculations. Such agreement can be achieved only when the spectra corresponding to different polarizations are summed and the influence of the apparatus is thus eliminated.

We can see that an investigation of the Zeeman splitting of the NP component of the luminescence due to excitons bound to phosphorus atoms in silicon, carried out in a wide range of magnetic fields using high-resolution apparatus, can give the values of the g factors of electrons and holes, which are in good agreement for the crystallographic directions $H \parallel [001]$ and $H \parallel [111]$. The constants representing the diamagnetic shift of the Zeeman components depend on the momentum of a hole in the initial state. The relative intensities of the Zeeman components are in satisfactory agreement with the results of calculations for the shell model of bound excitons, which demonstrates a quantitative agreement between the model and experiment.

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