Nonparabolicity and anisotropy of the electron energy spectrum in GaAs

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The electron energy spectrum in a quantizing magnetic field was studied by laser photoelectric magnetospectroscopy. The cyclotron-resonance (CR) line splitting due to conduction-band nonparabolicity was investigated. The splitting and position of the CR line doublet were found to depend on the magnetic-field orientation relative to the crystallographic axes. This effect is due to the conduction-band anisotropy. CR measurements were made for both free and localized shallow donor electrons. It is shown that failure to take the nonparabolicity and anisotropy into account can lead to wrong identification of the impurities by the photoelectric magnetospectroscopy method. Expressions for the electron-energy spectrum were obtained with account taken of the effect of the higher bands. Comparison of the theory with experiment yielded the parameters of the Hamiltonian to within terms of fourth order in **K·p** perturbation theory.

1. INTRODUCTION

Gallium arsenide is a cubic semiconductor with the conduction band minimum at the center of the Brillouin zone. The electron effective mass and the g-factor at the band minimum ($E = 0$) are isotropic. The dispersion law is assumed as a rule to be isotropic also at finite energy E. This approximation is justified by the usually small ratio of E to the conduction bandwidth, which made the anisotropy effects that exist at $E \neq 0$ unobservable in the spectroscopy of GaAs until recently. However, progress in the technology of production of ultrapure semiconductors[1] and the advent of high-sensitivity spectroscopic methods for their study[2] have uncovered the possibility of investigating subtle details of the electron spectrum. The anisotropy effects turn out here to be essential for the determination of the fundamental parameters of the energy spectrum. We report here an observed dependence of the shapes of electron CR spectra on the magnetic field orientation relative to the crystallographic axes. The good agreement between the experimental results and the theoretical estimates suggests that this effect is due to the electron-energy-spectrum anisotropy.

The CR line was observed[3–5] to split into two components. The splitting is attributed to conduction-band nonparabolicity. Indeed, with a nonquadratic dispersion, spin-orbit coupling makes the g-factors of the different Landau levels different, causing thereby the transition energies of electrons with opposite spin projections on the magnetic field **H** to be likewise different. We have observed changes in the splitting and position of the CR doublet as **H** was rotated relative to the crystallographic axes. The first and second of these effects are due to the g-factor and cyclotron-mass anisotropy, respectively. Comparsion with theory yielded the nonparabolicity and anisotropy parameters of the conduction band.

In Sec. 2 are presented equations for the electron-energy spectrum in a magnetic field, with account taken of the higher-band effects. The parameters of the Hamiltonian were calculated by the **K·p** perturbation theory. In Sec. 3 we describe the method used to study the CR spectra of the electrons, both free and bound to shallow donors, by laser high-resolution photoelectric magnetospectrometry. Section 4 deals with the measured position and splitting of the free electron CR line. A comparison with the theory has enabled us to obtain the parameters of the Hamiltonian. Section 5 is devoted to CR study of electrons bound to shallow donors. In strong magnetic fields the line splitting for donors with different chemical properties turned out to be comparable with the difference between their chemical shifts. It is shown that this fact must be taken into account when identifying the impurities.

These results were reported briefly elsewhere.[6]

2. FREE ELECTRON ENERGY SPECTRUM IN A MAGNETIC FIELD, WITH ALLOWANCE FOR THE EFFECT OF HIGHER BANDS

In a magnetic field, the energy spectrum of GaAs electrons near the bottom of the conduction band, is determined by the Hamiltonian[1)]

$$\begin{aligned}\mathcal{H}=&\hbar^2K^2/2m+{}^1/_2g\mu_B(\boldsymbol{\sigma}\mathbf{H})+a_1K^4+a_2(eH/\hbar c)^2\\&+a_3(\{K_x^2,K_y^2\}+\{K_x^2,K_z^2\}+\{K_y^2,K_z^2\})\\&+a_4K^2(\boldsymbol{\sigma}\mathbf{H})+a_5\{(\boldsymbol{\sigma}\mathbf{K}),(\mathbf{KH})\}\\&+a_6(K_x^2\sigma_xH_x+K_y^2\sigma_yH_y+K_z^2\sigma_zH_z),\end{aligned}$$

where $\hbar k$ is the kinematic momentum, $\boldsymbol{\sigma}$ are Pauli matrices, and μ_B is the Bohr magneton. The curly brackets denote the anticommutator. The x, y, and z axes are directed along the principal cyrstallographic directions. The Hamiltonian is accurate to within fourth-order terms of **K·p** perturbation theory.[7] The term of third-order in **K** (Ref. 8) is neglected because GaAs has no inversion symmetry (it will be shown below that its contribution is relatively small in a strong magnetic field). The set of invariants of the cubic symmetry group is restricted to the above terms in the order in question. The terms with the factors a_1 and a_3 are responsible for the energy dependence of the effective mass. The last three terms govern the energy dependence of the effective g-factor. The spectrum anisotropy is due to the

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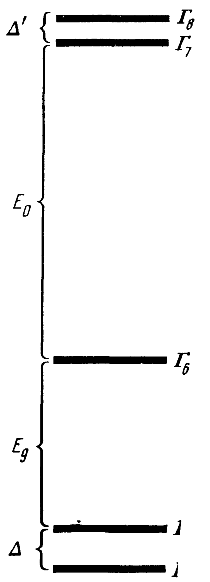

FIG. 1. Energy spectrum of electrons at the center of the Brillouin zone of GaAs at H = 0. The levels closest to the bottom of the conduction band (Γ_6) are shown. The subscripts of Γ designate the representations according to which the wave functions corresponding to these levels are transformed under operations of the symmetry group *Td*. (If the fact that the crystal has no inversion center is neglected, the parities of the states of the two upper levels and of the conduction band levels are the same and are opposite to the parities of the valence-band states).

terms proportional to a_3 and a_6. The term $a_2(eH/\hbar c)^2$ describes the diamagnetic shift of the conduction-band edge.

At moderate electron energies $E \ll 1$ eV (1 eV is the typical size of the energy gap) the spectrum of Hamiltonian (1) is determined primarily by the first two terms:

$$E_{N,k,\pm}=\hbar\omega_c=(N+{}^1/_2)+\hbar^2k^2/2m\pm{}^1/_2 g\mu_B H.$$

Here $\hbar\omega_c$ is the cyclotron energy, N the Landau-level number, k the wave vector of motion along **H**, and the ± signs refer to the different spin projections on the direction of **H**. Regarding the remaining Hamiltonian terms as a small perturbation, we obtain for the first-approximation correction to the energy of the $(N, k, \pm)$ level

$$a_1q^4(2N+1)^2+a_2q^4+{}^1/_2a_3\{q^4[(2N^2+2N-1)+3(2N^2+2N+1)f]+4k^2q^2(2N+1)(1-3f)+4k^4f\}\pm a_4H[q^2(2N+1)+k^2]\pm 2a_5Hk^2\pm a_6H[q^2(2N+1)f+k^2(1-2f)],$$

$$q^2=eH/\hbar c. \tag{2}$$

the factor

$$f=(H_x^2H_y^2+H_x^2H_z^2+H_y^2H_z^2)/H^4 \tag{3}$$

describes the dependence of the spectrum on the orientation of **H**.

We evaluate now the coefficients a_1–a_6 by **K·p** perturbation theory.[7] It could be used to find the exact values of the coefficients if the energies and wave functions of all states at **K** = 0 were known. We restrict ourselves, however, in the summation over the intermediate states to bands closest in energy to the conduction band (see Fig. 1). The closest is the valence band ($E_g \approx 1.52$ eV). Interaction with this band is known to result in a dependence of the effective mass and g-factor of the electron on its energy.[9–11] In no order of perturbation theory, however, does it cause anisotropy of the spectrum. In other words, if the conduction band interacted only with the valence band, the coefficients $a_3 - a_6$ would be zero. In addition, the coefficient a_5 would also be zero. To calculate these coefficients we take into account the coupling with the band lying $E_0 \approx 2.97$ eV above the bottom of the conduction band[12] (we denote it the c' band). We then obtain in fourth order of **K·p** perturbation theory[2)]

$$a_1=-\frac{\hbar c}{e}\left[\xi\frac{(3E_g^2+4E_g\Delta+2\Delta^2)(3E_g+2\Delta)}{E_g+\Delta}+2\chi\Delta^2\right],$$

$$a_2=-\frac{\hbar c}{e}\left[\xi\frac{\Delta^2(2E_g+\Delta)}{E_g+\Delta}+\chi(27E_g^2+36E_g\Delta+14\Delta^2)\right],$$

$$a_3=-6\frac{\hbar c}{e}\chi(3E_g^2+4E_g\Delta+\Delta^2),$$

$$a_4=\xi\Delta(9E_g+4\Delta)-\chi\Delta(6E_g+\Delta),$$

$$a_5=-\chi\Delta(3E_g+2\Delta),\qquad a_6=4\chi\Delta(3E_g+\Delta), \tag{4}$$

where

$$\xi=\frac{e\hbar^3}{36m_0^2c}\left(\frac{2|P|^2}{m_0}\right)^2\frac{1}{E_g^3(E_g+\Delta)^2},$$

$$\chi=\frac{e\hbar^3}{36m_0^2c}\frac{2|P|^2}{m_0}\frac{2|Q|^2}{m_0}\frac{1}{E_0E_g^2(E_g+\Delta)^2}$$

m_0 is the free-electron mass, and P and Q are the dipole-moment[9] matrix elements that relate the states of the valence band to those of the conduction and c' bands, respectively. $\Delta \approx 0.34$ eV is the energy of the spin-orbit splitting of the valence-band edge. The similar splitting Δ' of the c' band is disregarded because the corresponding correction is small ($\sim\Delta'/E_0$ for Eqs. (4), which is only a few percent at $\Delta \approx 0.17$ eV, Ref. 12). Equations (4) contain likewise no terms due to the fact that the GaAs crystal has no inversion symmetry (i.e., the matrix element of the dipole moment formed between the set of Bloch functions of the conduction and c' bands is nonzero). Their contribution to the coefficients $a_1 - a_6$ can be estimated to be less than or on the order of 10%. The corrections due to interaction with the higher bands should be of the same order of magnitude. The value $2|P|^2/m_0 \approx 29$ eV was obtained from an analysis of the experimental determinations of m and g. The value of $2|Q|^2/m_0$ can be estimated assuming the heavy-hole spectrum to be determined primarily by the interaction of the valence band with the c' band. Taking the expression for the tensor of the reciprocal of the heavy-hole effective mass from Ref. 15 and the experimental data from Ref. 16 we obtain $2|Q|^2/m_0 \approx 16$ eV. Substituting these values in (4) we arrive at

$$a_1,\, a_2,\, a_3 \approx (-2{,}9;\ -2{,}6;\ -1{,}7)\cdot 10^{-29}\ \text{eV}\cdot\text{cm}^4;$$

$$a_4,\, a_5,\, a_6 \approx (7{,}1;\ -0{,}8;\ 3{,}2)\cdot 10^{-23}\ \text{eV}\cdot\text{cm}^2\cdot\text{Oe}^{-1}$$

Finally, we discuss the effect exerted on the Hamiltonian spectrum by the term[8]

$$\alpha\frac{\hbar^3}{2m(2mE_g)^{1/2}}[\sigma_x(K_yK_xK_y-K_zK_xK_z)+\sigma_y(K_zK_yK_z-K_xK_yK_x)+\sigma_z(K_xK_zK_x-K_yK_zK_y)], \tag{5}$$

TABLE I. Characteristics of GaAs samples.

Sample No.	N_D-N_A, cm^{-3}	μ_{77}, cm^2·V^{-1}·s^{-1}	μ_{300}, cm^2·V^{-1}·s^{-1}	Orientation of normal to layer	Chemical makeup of shallow donors
1	$6\cdot10^{13}$	170 000	8400	[001]	X_1, D, X_2, X_3
2	$8\cdot10^{14}$	100 000	8000	[001]	D, X_2

which has not yet been taken into account. Experiment[17] yields for GaAs a constant $\alpha\approx6\cdot10^{-2}$. The presence of this term in the Hamiltonian is due to absence of an inversion center in the crystal. In a zero magnetic field this results in a conduction-band spin-orbit splitting proportional to K^3. The splitting depends on the orientation of the vector **K** (thus, it is zero for $\mathbf{K}\|(111)$, $\{100\}$). Therefore at small **K** the nonparabolicity and corrugation of the conduction band are due primarily to the interaction (5). The Hamiltonian terms considered above are proportional to K^4 and make thus only a negligible contribution. On the contrary, in strong magnetic fields the contribution of term (5) turns out to be small compared with that of (2). Indeed, one readily sees that the term (5) contributes to the energy only in second-order perturbation theory. The H-dependence of the correction to the energy is then the same as in (2), i.e., quadratic (at $k=0$). It will be shown below, however, that the contribution of (5) is numerically small.

It should be calculated nonetheless, since it has a different orientational dependence.

Consider now a more interesting case, when the cyclotron energy $\hbar\omega_c$ is much higher than the charactristic energy of interaction (5). In GaAs, the spin splitting energy is $|g|\mu_B H \ll \hbar\omega_c$ ($|g|m/2m_0\approx1.5\cdot10^{-2}$). We therefore neglect initially the virtual transitions with change of the Landau-level number but take strictly into account the transitions between the spin-doublet states. This yields for the spin splitting of the Nth level:

$$\left\{(g\mu_B H)^2+\alpha^2\frac{\hbar^6}{2m^3E_g}\left[k^3-3kq^2\left(N+\frac{1}{2}\right)\right]^2(f-9f')\right\}^{1/2}, \tag{6}$$

$$f'=H_x^2H_y^2H_z^2/H^6.$$

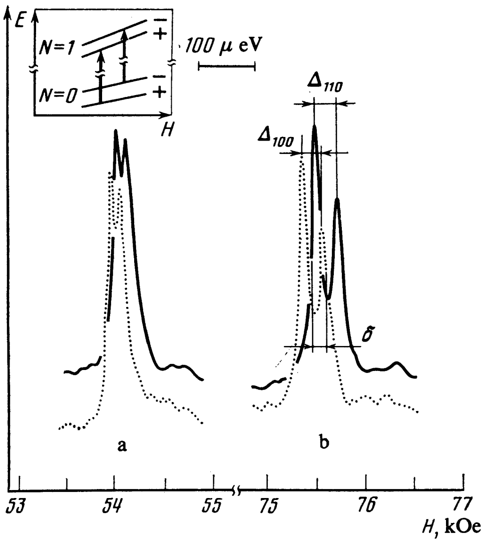

FIG. 2. CR lines in the photoconductivity center: a) $\hbar\omega=9.3$ meV, b) $\hbar\omega=12.85$ meV. Solid lines— $\mathbf{H}\|[110]$, dashed—$\mathbf{H}\|[100]$; sample No. 1; $T=4.2$ K. Inset—scheme of transitions corresponding to the CR-line doublet.

We can see, however, that the contribution of (5) to this expression vanishes at $k=0$. For small k we must therefore consider the transitions with change of N (since the ratio $|g|m/2m_0$ is small, the result (6) is wrong only very close to the bottom of the Landau band). As seen from (5), in second-order perturbation energy the band N interacts at $k=0$ only with bands $N\pm1$ and $N\pm3$. We arrive thus at the following expression for the correction of the energy of the state (N, $\pm$, $k=0$):

$$\alpha^2\frac{\hbar^6}{8m^3E_g}\left(\frac{eH}{\hbar c}\right)^3\left\{-\frac{[(N+1)^3-N^3](f-9f')}{8\hbar\omega_c}\right.$$
$$-\frac{3[(N+3)(N+2)(N+1)-(N-2)(N-1)N](f-f')}{8\hbar\omega_c}$$
$$\mp\frac{18\begin{pmatrix}(N+1)^3\\ N^3\end{pmatrix}f'}{\hbar\omega_c-g\mu_B H}$$
$$\pm\frac{\begin{pmatrix}N^3\\ (N+1)^3\end{pmatrix}(1-4f+9f')}{2(\hbar\omega_c+g\mu_B H)}$$
$$\left.\mp\frac{\begin{pmatrix}(N+3)(N+2)(N+1)\\ (N-2)(N-1)N\end{pmatrix}(1-4f+9f')}{2(3\hbar\omega_c-g\mu_B H)}\right\}. \tag{7}$$

The upper sign and the upper row in the grouping $\begin{pmatrix}\cdots\\ \cdots\end{pmatrix}$ refer to the state (N, $+$), and the lower sign and lower line to the state (N, $-$). In the case of GaAs we can let $g\to0$ in the denominators. As seen from a comparison of (7) and (2), the contribution of (7) is small compared with that of (2). Indeed, its relative contribution to the CR- line spin-splitting anisotropy is $\sim10^{-2}$, and is even smaller, 10^{-3}, to the anisotropy of the cyclotron mass. The only case when the anisotropy associated with (5) can be important is if **H** rotates in the (111) and similar planes. The function f [Eq. (3)] is unchanged by such orientation variations, so that the correction (2) is also constant.

3. EXPERIMENTAL

The electron CR in GaAs was studied with a submillimeter laser magnetic spectrometer having a resolution of $\sim1\ \mu$ eV (Ref. 18). The photoconductivity spectra were obtained in a magnetic field $H\leqslant85$ kOe at $T=4.2$ K. The photoresponse was obtained at fixed radiation frequencies by sweeping the magnetic field of a superconducting solenoid.

Conventional lock-in detection was used, the radiation being amplitude-modulated with a chopper at 750 Hz. The radiation ($\hbar\omega = 3.68 - 17.59$ meV) was generated by submillimeter cw gas lasers. The H_2O-D_2O and HCN lasers (see Ref. 18) were supplemented in the present work with a CH_3OH laser pumped by a tunable CO_2 laser. The lasers operated at a power level 1–30 mW. In some cases the measurement sensitivity was enhanced by employing additional unmodulated intrinsic illumination.

We studied pure n-GeAs layers grown by gas-transport epitaxy on a semiconducting GaAs substrate. The CR features revealed were observed in all 11 samples studied (see Secs. 4 and 5). The characteristics of the two samples whose photoconductivity spectra will be described in Secs. 4 and 5 are listed in Table I.

The magnetic field was applied along the layer surface perpendicular to the direction of light propagation (Voigt geometry). The samples were rotated by a special unit that kept the normal to their surfaces parallel to the radiation-propagation vector. The external electric field chosen was much weaker than needed for impurity impact ionization and was a few V cm^{-1}.

4. FREE-ELECTRON CYCLOTRON RESONANCE

Figure 2 shows two photoconductivity-spectrum segments corresponding to the CR lines. Spectra a and b were obtained at different laser frequencies. The solid lines correspond to the orientation $\mathbf{H}\|[110]$ and the dashed to $\mathbf{H}\|[100]$. The CR lines are split into two components, each corresponding to the spin-conserving electron transition from the zeroth to the first Landau level. The splitting, as illustrated by the inset of Fig. 2, is caused by the energy dependence of the electron g-factor, i.e., by the differences between the Zeeman splittings of the different Landau levels. As the sample was rotated in the (001) plane the splitting $\Delta(\mathbf{H})$ ranged from a minimum value (Δ_{100} at $\mathbf{H}\|[100]$ to a maximum (Δ_{100}) at $\mathbf{H}\|[110]$. A shift $\delta(\mathbf{H})$ of the doublet-center position was also observed. The field strength H corresending to the doublet center increased (meaning that the cyclotron energy decreased) as the orientation was varied from $\mathbf{H}\|[100]$ to $\mathbf{H}\|[110]$. Figure 3 shows the angular dependence of $\Delta(\mathbf{H})$ and $\delta(\mathbf{H})$. It has a period $\pi/2$ if $\mathbf{H}$ rotates in the (001) plane. If the rotation is in the (111) plane, however, the anisotropies of the splitting and of the line shift lie within the experimental errors.

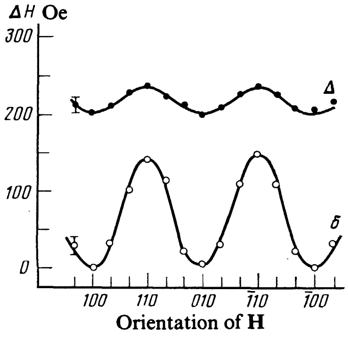

FIG. 3. Splitting Δ and doublet-center shift δ of CR line vs magnetic-field orientation relative to the crystal axes. H is in the (001) plane (sample No. 1; $\hbar\omega = 12.85$ meV, $T = 4.2K$).

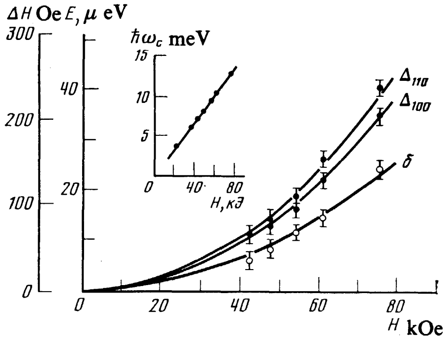

FIG. 4. Splitting Δ and shift δ of CR line vs magnetic field intensity. Inset—dependence of cyclotron energy $\hbar\omega_c$ on H.

Figure 4 illustrates the increase of Δ and δ with increasing magnetic field and shows it to be close to quadratic. At the maximum field $H\approx 80$ kOe, typical values of Δ and δ reach several times ten μ eV [in the conversion to energy units we used the experimentally determined dependence of the cyclotron energy on the magnetic field (inset of Fig. 4)].

The quantities Δ and are defined as

$$\Delta=(E_{1,+}-E_{0,+})-(E_{1,-}-E_{0,-}),$$

$$\delta={}^1/_2(E_{1,+}+E_{1,-})-{}^1/_2(E_{0,+}+E_{0,-})$$

(the energies should be taken at $k = 0$). By virtue of (2) we have

$$\Delta=4(a_4+a_6f)(eH/\hbar c)H, \qquad \delta=6a_3(eH/\hbar c)^2f.$$

The angular dependence thus derived agrees with experiment. Indeed, the function f varies, when $\mathbf{H}$ is rotated in the (001) plane, from zero at $\mathbf{H}\|[100]$ to a maximum value 1/4 at $\mathbf{H}\|[110]$ and remains unchanged (and equal to 1/4) as the field rotates in the (111) plane. The best experimental fit of the theoretical plots of the CR line splitting and shift vs the magnitude and orientation of $\mathbf{H}$ is obtained for

$$a_3=-1{,}2\cdot10^{-29}\ \text{eV}\cdot\text{cm}^4,\quad a_4=9{,}7\cdot10^{-23}\ \text{eV}\cdot\text{cm}^2\cdot\text{Oe}^{-1},$$

$$a_6=4{,}9\cdot10^{-23}\ \text{eV}\cdot\text{cm}^2\cdot\text{Oe}$$

(the coefficient errors due to the limited number of experimental points are less than 10%). The estimates presented in Sec. 2 differ from these values by 30–40%.

5. IMPURITY CYCLOTRON RESONANCE

Figure 5 shows photoconductivity-spectrum sections in the impurity CR region ($1s \to 2p_{+1}$ shallow donor photoexcitation lines). Spectra a and b correspond to different photon energies. The three strongest lines are due to excitation of three chemically different donors ($X_1 = Se$, $X_2 = S$, $X_3 = Ge$, according to the identification of Refs. 19 and 20). The weak line is due to an Sn impurity.[3)] In a sufficiently strong magntic field (Fig. 5b) each line is split into a doublet (just as in the case of the free-electron CR). In the magnetic field corresponding to Fig. 5a the effects are partially masked by the widths of the individual line components. Thus, no line splitting is observed for $\mathbf{H}\|[100]$. At $H\leqslant 30$

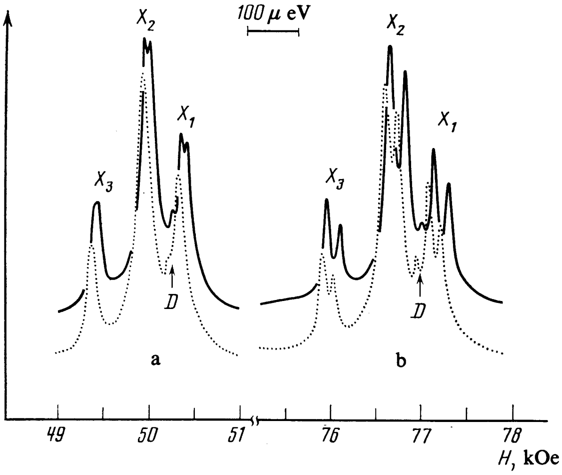

FIG. 5. Shallow-donor photoexcitation spectra ($1s \to 2p_{+1}$ transition): a) $\hbar\omega = 12.85$ meV; b) $\hbar\omega = 17.59$ meV. Solid lines—H‖[110], dashed—H‖[100]. The letters denote the lines of donors of different chemical elements (sample No. 1, $T = 4.2$ K).

kOe, however, no splitting and shift of impurity CR lines is seen even in the purest samples. The dependences on the orientation and on the magnetic field strength are shown in Fig. 6.

Several features of the observed spectra are noteworthy. The light circles in Fig. 7 show the magnetic field dependences of the chemical shift differences of donors D, X_2, and X_3 relative to donor X_1. The magnetic field increases the electron density in the central cell. As a result, the chemical shifts and their differences increase with increasing H. The filled circles denote the magnetic-field dependences of the line splittings. The most interesting is the following circumstances. In a field $H \sim 100$ kOe ($\gamma = \hbar\omega_c/2\text{Ry} \sim 1$, where Ry is the effective Rydberg), the splitting Δ becomes comparable with the chemical-shift difference. As can be seen from the figure, the value of Δ at $H > 70$ kOe exceeds the shift difference of donors X_1 and D. As a result, line components of donors with different chemical properties turn out to lie between line components of one donor (see inset of Fig. 7).

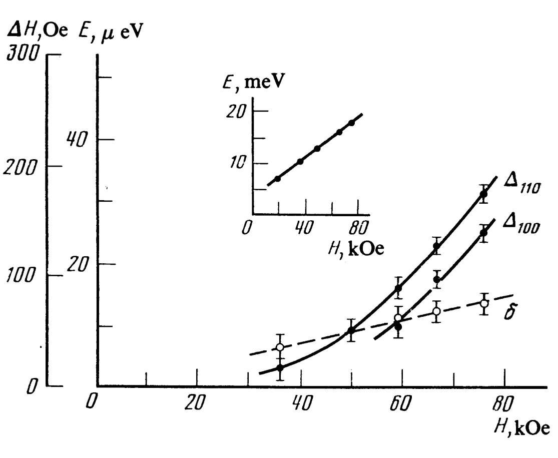

FIG. 6. Splitting Δ and shift δ of the $1s \to 2p_{+1}$ transition line of the donors X_2, D, and X_1 vs the magnetic field strength. Inset—dependence of the transition energy on H.

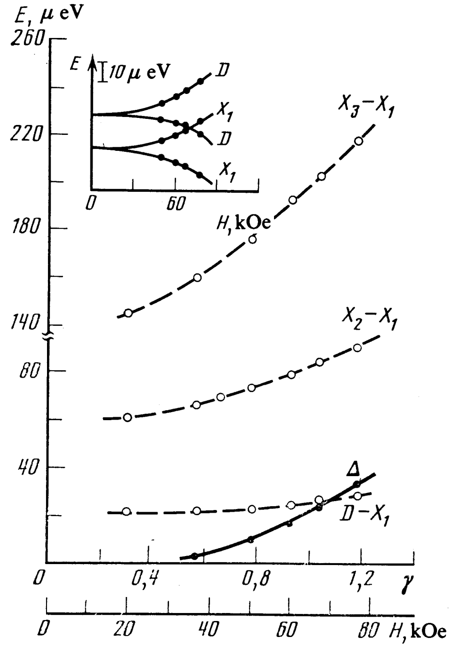

FIG. 7. Magnetic-field dependences of the differences of the chemical shifts of the donors D, X_2, and X_3 relative to the donor X_1 (light circles), and splittings of the $1s \to 2p_{+1}$ photoexcitation lines (dark circles) of the donors X_2, D, and X_1 at H‖[110] ($\gamma = \hbar\omega_c/2\text{Ry}$). Inset—dependences of the spacings between the photoexcitaiton line components of the donors X_1 and D at H‖[110].

This point should be taken into account when identifying impurities by photoelectric magnetospectroscopy.

Note that Figs. 5a (solid curve) and 5b show clearly only one doublet component of the weak D line. Its reliable identification as one of the doublet components follows from a comparison of the spectra of Fig. 8. Spectrum 1 was obtained

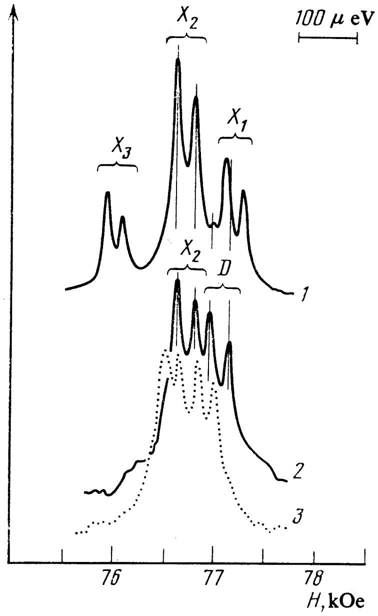

FIG. 8. Photoexcitation spectra of shallow donors (transition is $\to 2p_{+1}$). 1—sample No. 1: 2, 3—sample No. 2. Solid curves—H‖[110], dashed—H‖[100] ($\hbar\omega = 17.59$ meV, $T = 4.2$ K).

with the same sample as in Fig. 5, while spectrum 2 pertains to the sample in which X_2 and D are the predominant impurities (the orientation of **H** relative to the crystal axes is the same in both cases). Figure 8 demonstrates particularly clearly of the importance of proper **H** orientation to the identification of impurities. Curves 2 and 3 were obtained at different orientations. A change of orientation is seen to cause a shift of the spectrum by an amount comparable with the difference in the chemical shifts of the nearest donors.

The splittings of the X_1, X_2, and D lines are close in magnitude, but the X_3 line is an exception. Its splitting is 20–25% smaller and the anisotropy is greater by the same amount. At the same time, the binding energies of all the above donors are almost equal, differing only by a few percent. This could be explained by assuming that deep resonance levels of impurity X_3 exist under the minima of the lateral L (or X) valleys, and are close in energy to the conduction-band bottom. The energy spacing between these resonance levels and those of the energy separation between these resonance levels and the levels of the Γ valley should decrease with increasing magnetic field. The resulting anticrossing of the levels should cause the donor X_3 to behave differently from the other donors. This difference was observed earlier in studies of the influence of hydrostatic compression and of a magnetic field on the donor spectrum in GaAs (Ref. 21) (compression likewise leads to anticrossing). One can conclude from Ref. 21 that in the absence of compression the resonance levels have an unusually litte effect on the Γ-valley spectrum even in fields $H \sim 100$ kOe. This explains in fact the small difference between the chemical shifts. The nonparabolicity and anisotropy of the spectrum (which by themselves are very small) should, however be influenced much more strongly by the resonance levels. They are then quite capable of competing with the influence of the higher bands.

We point out in conclusion that the calculations of Sec. 2 can be readily extended to the case of an electron moving in the field of an impurity center. In a strong magnetic field, when the influence of the higher bands can be taken into account by perturbation theory, it suffices: (1) to make in Eq. (2) the sustitution

$$q^2(2N+1) \to \mathbf{K}^2_\perp, \quad k^2 \to \mathbf{K}_\parallel{}^2,$$

where $\mathbf{K}_\perp$ and $\mathbf{K}_\parallel$ are the operators of the kinematic momenta transverse and parallel to the magnetic field, respectively; (2) to average the result over the state of the unperturbed Hamiltonian. The final answer is expressed in terms of the averaged values $\langle \mathbf{K}_\perp^2 \rangle$, $\langle \mathbf{K}_\parallel^2 \rangle$, $\langle \mathbf{K}_\perp^4 \rangle$, $\langle \mathbf{K}_\parallel^4 \rangle$ and $\langle \mathbf{K}_\perp^2 \mathbf{K}_\parallel^2 \rangle$. The relations calculated in this way agree qualitatively with the measurements. A direct comparison, however, is difficult. The point is that the determination of these averages for magnetic fields in which the cyclotron energy is of the order of the Bohr energy calls for computer calculations.

1) Strictly speaking, the Landau levels should broaden even in a perfect crystal (because the electron energy depends on the position of the center of orbit in the unit cell). This broadening is small and is neglected here.

2) Note that the parameters of the Hamiltonian (1) were calculated earlier[13] for $\Delta \gg E_g$. In this limiting case, however, our results differ from those in Ref. 13 by numerical factors.

3) The shallow donors were identified by the spectra of the $1s \to 2p_{+1}$ transition lines at the wavelength 118.8 μm ($\hbar\omega = 10.44$ meV), by using a specially calibrated superconducting solenoid with $H \lesssim 50$ kOe. The spectra presented in Secs. 4 and 5 for $H \gg 50$ kOe were obtained with another solenoid for which the values of H corresponding to the line maxima were determined with a larger error (up to 0.3%).

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