Linear and quadratic Zeeman effect of excitons bound to neutral acceptors in GaSb†

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(Received 26 December 1974)

The linear and quadratic Zeeman effect of four different excitonic recombination lines at 805.4, 803.4, 800.1, and 796.1 meV are investigated. The decay of excitons bound to neutral acceptors (A^0, X) is responsible for these lines. The angular momentum J of the (A^0, X) ground state is in at least three cases 1/2 and not 3/2 or 5/2. The sixfold linear Zeeman splitting of the different lines is dominated by the same large value $g_{\text{eff}} = -8.95 \pm 0.15$ of the initial state of the transition. It is shown that the average diamagnetic shift of a deep (A^0, X) complex is described satisfactorily by Larsen's theory of a donor in a magnetic field. These findings suggest that the (A^0, X) bound exciton may be described by a donorlike A^+ center binding an electron. From the splitting of the final states (neutral acceptors), the g values of the bound holes are determined to be $K = 0.14$–0.25 for the different acceptors. A recently predicted diamagnetic splitting Δ of the acceptor states having $|m_j| = 1/2$ and 3/2 is observed.

I. INTRODUCTION

The analysis of the radiative recombination in high magnetic fields of excitons bound to different neutral acceptors of varying depth is a useful means to investigate the electronic structure of the initial state of the transition (A^0, X), as well as the final state, the neutral acceptor A^0.[1] Different basic features of both states are still not very well understood.

Some of the open questions concern the form of the potential of a deep impurity and the wave function of a charge carrier trapped in such a potential.[1,2] Related to this question is the attempt to establish experimentally in different materials which of the possible eigenstates of (A^0, X) $(J = \frac{1}{2}, \frac{3}{2}$, or $\frac{5}{2})$ has the lowest energy. The last question gained some importance because for several deep acceptors in[3–5] GaAs and[6] GaSb, the experimentally established angular momentum of the ground state of an (A^0, X) complex was found to be $J = \frac{1}{2}$. A $J = \frac{1}{2}$ ground state is in contradiction to the theory of atomic spectra which predicts the $J = \frac{3}{2}$ or $\frac{5}{2}$ states to have the lowest ground-state energy.[1,4] Only for the most shallow (A^0, X) complexes in GaAs and InP a $J = \frac{1}{2}$ ground state could be excluded experimentally.[7]

Until recently, no theory of the first- and second-order Zeeman effect of acceptor states in terms of band-structure parameters was given. A first attempt to establish such a theory[8] uses a Coulomb potential as attractive potential for the hole. This description might not be sufficient for acceptors deeper than the effective-mass acceptor. But at least some of the qualitative predictions should hold also for deep centers. One of the most important predictions is a diamagnetic splitting of the $|m_j| = \frac{1}{2}$ and $\frac{3}{2}$ acceptor states.

In this paper we investigate the influence of magnetic fields up to 10 T on the luminescence spectra of four (A^0, X) complexes with very different binding energies. From the splitting of the lines in a magnetic field, the angular momentum of the initial (A^0, X) state is unambiguously identified and the g values of the initial and final states are evaluated. The magnetic properties of a deep (A^0, X) complex is discussed in analogy to a neutral donor. The g values of the acceptor holes and their experimentally demonstrated diamagnetic splitting are compared with the predictions of the above-mentioned theory of acceptors in magnetic fields.[8] Finally, the validity of Haynes's rule[9] for the system investigated here is discussed. This rule predicts a proportionality between the localization energy E_B of an exciton and the ionization energy E_A of the binding acceptor.

II. EXPERIMENTAL

A. Samples

The experiments were carried out partially on epitaxial layers which were grown by liquid-phase epitaxy[10] (LPE) and partially on bulk crystals which were solution grown.[11] The surface of the epitaxial layers had a (100) orientation. Table I compiles some properties of typical crystals which were used. All samples were not intentionally doped.

B. Measurement technique

The samples were either immersed in liquid helium or mounted on a holder in an insert cryostat, temperature controlled by helium-gas flow. The magnetic field up to 10 T was produced by a superconducting split-coil magnet. Both Faraday- and Voigt-configuration experiments were possible. The π spectra were taken in Voigt configuration,

TABLE I. Properties of some of the crystals used for the experiments reported here.

Crystal No.	Growth process	$n_A - n_D$ (cm^{-3})
Wk 32	LPE	$<10^{16}$
Wk 33	LPE	$<10^{16}$
W 7	solution grown (bulk)	2×10^{17}
W 15	solution grown (bulk)	2.5×10^{16}

whereas the right-circularly-polarized (RCP) and left-circularly-polarized (LCP) spectra were taken in Faraday configuration. The luminescence was excited by a krypton laser with 500-mW maximum power. In order to avoid too strong interactions between the photo-created carriers, only excitation intensities of $\simeq 5\times10^2$ W/cm^2 were used. The emitted light was dispersed by a 60-cm Jobin-Yvon spectrometer and detected by a cooled (190 K) PbS cell. The linear polarizer was a HR-Polaroid foil, and $\lambda/4$ plates for the wavelength of the emitted light were constructed by combining several plastic retardation sheets. A more detailed description of the setup can be found in Ref. 1.

III. RESULTS

In this section we present spectra of bound exciton lines with and without applied magnetic field at various temperatures and in different crystals. The data deduced from these spectra will be used in Sec. IV for the identification of the lines discussed here and for the evaluation of the parameters of the linear and quadratic Zeeman effect.

Figure 1 shows the zero-field spectra of a solution-grown (W 15) and an epitaxial sample (Wk 32). In order to avoid misunderstandings which may arise from previous assignments of emission lines, we introduce a new nomenclature characterizing each bound exciton line with BE and a number, starting with BE_1 at the highest energy. Table II presents the spectral positions of the different lines discussed in this paper, together with the new and some previous assignments.

The spectra of the LPE layers (Wk...) and of the solution-grown bulk crystals (W...) differ considerably from each other. For instance, sample Wk 32 exhibits much more structure in the high-energy region: The shallower bound excitons BE_1 and BE_2 obviously dominate. This is in contrast to the spectrum of the solution-grown crystal W 15 where at zero field and low-excitation level, only the bound exciton BE_4 can be observed. A detailed discussion of the zero-field behavior of the different lines will be given elsewhere.[12]

The spectra of sample Wk 32 at a magnetic field of 10 T are given in Fig. 2 for different polariza-

TABLE II. Energetic position at $H=0$ and $T\simeq4.2$ K, present and former assignments of the lines reported in this paper. Localization energy of the bound excitons E_B at $H=0$. Isotropic g values K for the different bound holes for an orientation $\vec{H}\parallel\langle100\rangle$. Difference Δ in the diamagnetic shift (diamagnetic splitting) of the $|m_j|=\frac{3}{2}$ and $|m_j|=\frac{1}{2}$ hole states given in meV at the maximum field of 10 T. It must be pointed out that the two lines labeled by an asterisk are not identical with the line BE_2. Both lines β^* and D^* were measured at higher temperatures and therefore are not due to the decay of bound excitons: In some LPE samples, line BE_2 disappears with increasing temperature and a new line at about the same energy appears. A more detailed discussion of these lines will be given in d.

Spectral Position at $H=0$ and $T\simeq4.2$ K in meV		805.4 ± 0.2	803.4 ± 0.2	800.1 ± 0.2	796.1 ± 0.2
Assignment according to reference	present	BE_1	BE_2	BE_3	BE_4
	a	β			γ
	b		D^*		BE
	c		β^*		γ
Localization energy E_B of the exciton ($E_x=809.9$ meV[a,d])		4.5 ± 0.2	6.5 ± 0.2	9.8 ± 0.2	13.8 ± 0.2
K ($\vec{H}\parallel\langle100\rangle$)		0.14 ± 0.03	0.19 ± 0.03	...	$0.25^{+0.05}_{-0.1}$
Δ(meV) at 10 T		0.024 ± 0.015	0.08 ± 0.04	...	...

[a] See Ref. 18.
[b] See Ref. 11.
[c] C. Benoît à la Guillaume, P. Lavallard, Phys. Rev. B 5, 4900 (1972).
[d] See Ref. 12.

tions. In this sample a splitting into two components can clearly be resolved for the lines BE_1 and BE_2. The same is true for line BE_4 in sample W 15. Each of these components shows an additional "triplet fine structure": The components shift slightly in their energetic position when the polarization is changed from $\vec{E} \parallel \vec{H}$ (π) to RCP or LCP: The dashed vertical lines in Fig. 2 represent the energetic positions of the π components. It can be seen that the RCP lines lie at somewhat higher and the LCP lines at somewhat lower energy. The energy difference between a LCP and a RCP component of the lines BE_1 and BE_2 is more clearly depicted in Fig. 3 at a field of 10 T. So, in fact, a splitting into *six* components for all three lines BE_1, BE_2, and BE_4 could be experimentally detected. This is a very instructive example of how useful it is to take spectra in Faraday as well as in Voigt configuration. The higher-energy components of line BE_3 are hidden by the lower-energy components of BE_1 and BE_2 at high magnetic fields. However, at low magnetic fields (2 T), an identical splitting as in the case of the other bound excitons, can be observed for BE_3. Furthermore, the variation of the $BE_3\uparrow$ component at higher fields is analogous to that of the $BE_1\uparrow$, $BE_2\uparrow$, and $BE_4\uparrow$ components, so that an identical decay mechanism for all the four lines can be assumed. The symbols $\uparrow$ and $\downarrow$ label the spin-up and spin-down states of the initial states of the transitions, as will be shown in Sec. IV A. The rough features of the Zeeman spectra are therefore about the same for all three dif-

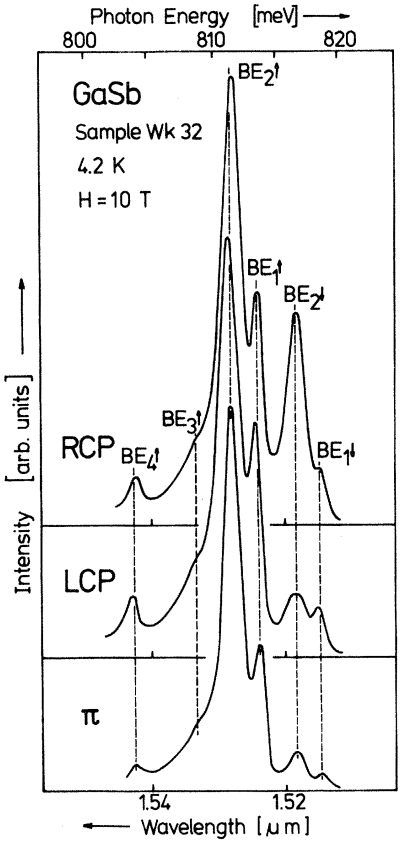

FIG. 2. Spectra of the sample Wk 32 at a field of 10 T and at different polarizations. The dashed vertical lines, represent the energetic position of the lines in π polarization. $\uparrow$ and $\downarrow$ indicate the orientation of the spin of the initial state of the transition relative to the magnetic field.

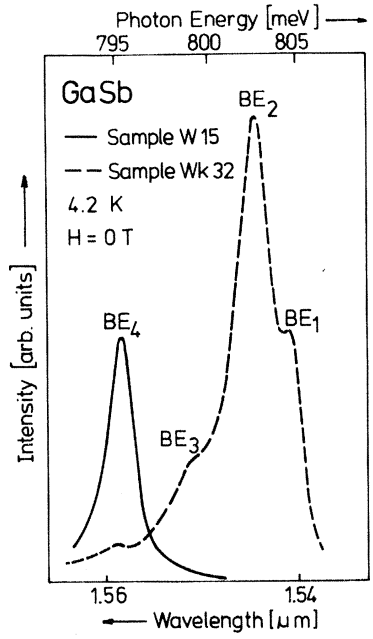

FIG. 1. Zero-field spectra of one solution-grown sample (W 15) and one epitaxial layer (Wk 32) at 4.2 K.

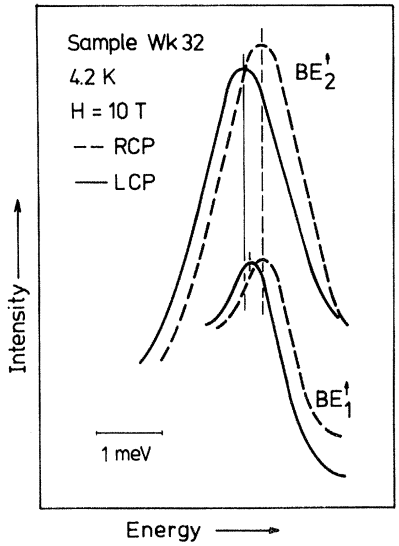

FIG. 3. Energy difference between the RCP$\uparrow$ and LCP$\uparrow$ components of the lines BE_1 and BE_2. The energy difference between the RCP and LCP components is approximately equal to 2 K (see text), where K is the isotropic hole-splitting parameter.

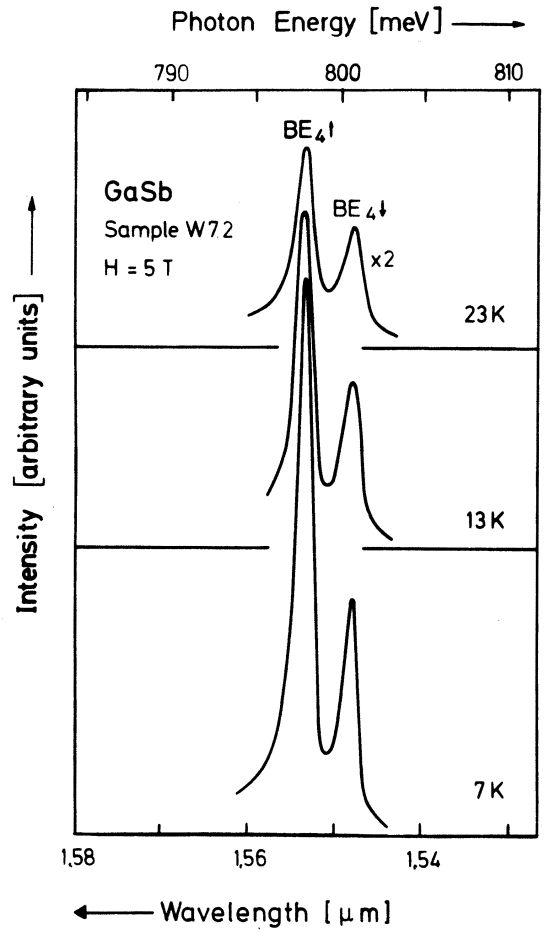

FIG. 4. Luminescence line BE_4 of the solution-grown sample W 7.2 in a field of $H=5$ T at three different temperatures: $T=7$, 13, and 23 K. The intensity at 23 K is multiplied by a factor of 2. The light was unpolarized.

ferent bound exciton lines BE_1, BE_2, and BE_4, and probably also for line BE_3.

The relative intensity of the various components of the same line depends on magnetic field strength, temperature, and polarization in the following way:

(a) By increasing the magnetic field, the low-energy components gain intensity.

(b) By decreasing the temperature, the low-energy components gain intensity too. This behavior is demonstrated in Fig. 4 for line BE_4 for temperatures between 7 and 23 K at a magnetic field of 5 T. Though the relative intensities of the two components do not follow a Boltzmann law, obviously a certain thermalization took place.

(c) From Fig. 2 it can be seen (for example, for the case of line BE_2) that the RCP component $BE_2\downarrow$ is more intense than the LCP $BE_2\downarrow$ component. The $BE_2\uparrow$ components behave in an opposite way: Here the RCP component is weaker than the LCP. Unfortunately, it is not possible to determine very precisely the intensity ratios of the different components of the same line from these spectra because of the strong overlap of the different lines.

Besides the splitting the BE lines undergo due to the linear Zeeman effect, they are shifted nonlinearly by the magnetic field due to a diamagnetic effect. The center of gravity is found to be shifted in a different way for the three corresponding pairs of components. Details of this unexpected behavior will be discussed in Sec. IV C after an analysis of the Zeeman pattern, which will be done in Sec. IV B. Before we proceed to this point, we shall identify unambiguously the BE lines due to the recombination of excitons bound to neutral acceptors.

IV. DISCUSSION

A. Identification of the initial and final states of the transitions

Figure 4 shows a pronounced drop of the over-all intensity of the line BE_4 from 7 to 23 K. At temperatures larger than 35 K, this line becomes undetectable. The other lines show qualitatively the same drop of intensity at already lower temperatures. The small ionization energies which can be derived from this temperature dependence[12] rule out a recombination of free electrons with holes bound to neutral acceptors, (e, A^0). (e, A^0) transitions can be detected separately at *higher* temperatures, as can be clearly seen from Fig. 2 of Ref. 13.

The temperature dependence of the BE lines holds also as an argument against a donor-acceptor pair transition: Such a transition should disappear at about 30 K (Ref. 13) and convert into the corresponding (e, A^0) recombination at higher energy. This is experimentally not observed for the BE lines. Therefore, we can rule out (e, A^0)—as well as (D^0, A^0)—recombinations to be responsible for the lines BE_{1-4}. A discussion of the half-widths[12] of the lines, as well as the shift of their center of gravity with magnetic field, confirm that they are due to bound exciton decay.

Let us now raise the question concerning the nature of the center binding the exciton. One possibility for the binding center is a neutral donor D^0. This possibility is *a priori* very unlikely because the localization energies E_B of these excitons should be much smaller for effective-mass donors in GaSb. The energies E_B of BE_{1-4} are given in Table II. The splitting in this case should give about the g factor of the free electrons due to the splitting of the final state, the neutral donor. But the experimental observation of the strong thermalization into the $\uparrow$ components proves that the observed large splitting is caused by the initial state. So the possibility of (D^0, X) decay can be excluded definitely. With similar arguments, ionized donors can be excluded as binding centers. As possible binding centers, only isoelectronic impurities I and neutral acceptors

A^0 remain. It is known that the isoelectronic group-III impurities cause no bound states in the usual III-V compounds. From the large diamagnetic shift (see Sec. IV C) of the bound excitons, one can exclude that the more electronegative group-V elements N, P, and As act as binding centers: In this case, the diamagnetic shift should be smaller than that of a donor, because the electron should be more localized and the diamagnetic shift of the hole is smaller too. Bi cannot absolutely be excluded by these arguments. But it is unknown whether Bi can act at all as an isoelectronic center in GaSb, because it has the same electronegativity as Sb. Therefore, we believe it to be improbable that one of the BE lines is caused by (Bi, X) decay. (A^0, X) complexes are the only remaining possibility. For the *deep* acceptors Sn and Cu in GaAs, it has been found that a $J=\frac{1}{2}$ state is the lowest of the three possible initial states of (A^0, X) with $J=\frac{5}{2}$, $\frac{3}{2}$, and $\frac{1}{2}$, achieved by j-j coupling of two holes with $j=\frac{3}{2}$ and one electron with $\frac{1}{2}$.[3-5] The state of lowest energy was found to have $J=\frac{5}{2}$ in the case that a *shallow* acceptor is acting as an exciton binding center in GaAs and InP.[7] This level inversion between shallow and deep binding centers can be explained as follows[15]: The coupling of the hole angular momentum to the local Stark field surrounding an acceptor could, for deep acceptors, give rise to a strong interaction between the $J=0$ two-hole state and the $m_j=0$ component of the $J=2$ two-hole state. As a consequence, the total angular-momentum state with $J=0$ lies energetically below $J=2$. Including electron spin, a $J=\frac{1}{2}$ state lies lowest, a fact which does not agree with normal theory of atomic spectra.[16] For a more detailed discussion of this effect, we refer to Refs. 1 and 7.

Therefore, we have to investigate which of the three possible states acts as an initial state for the transition. For an initial state with $J=\frac{3}{2}$ (or $J=\frac{5}{2}$), we would expect four π and six σ lines (or four π and eight σ lines) with splittings different from the ones observed.[1] For an initial state with $J=\frac{1}{2}$, we expect two π and four σ lines, where the main splitting of each pair of lines is dominated by the large electronic g_e value. This latter prediction agrees exactly with the observed splitting of all four BE lines. We concluded, therefore, that the lines BE_{1-4} are caused by the radiative recombination of excitons bound to neutral acceptors with a $J=\frac{1}{2}$ state as the initial state. In addition, we remark that the binding centers in all four cases (less established for BE_3) have lattice symmetry and are not complexes with somewhat lower symmetry, in which case we would expect a quite different splitting behavior and polarization pattern.[1,5] It would be quite natural now to proceed in discussing the acceptors acting as possible binding centers. We postpone this discussion to Sec. IV D to include the quantitative information about the different g values and diamagnetic susceptibilities.

B. Linear Zeeman effect

Figure 5 shows the group-theoretical splitting pattern of a $J=\frac{1}{2}\rightarrow J=\frac{3}{2}$ transition in a magnetic field. The initial state is a $J=\frac{1}{2}$ state (or Γ_6 state in Koster's notation), which was shown in Sec. IV A to be the lowest-energy eigenstate of the bound exciton. The spin Hamiltonian of this state is

$$\mathcal{H}=g_{\text{eff}}\mu_B\vec{S}\cdot\vec{H}\,, \tag{1}$$

where $\vec{S}$ is the angular momentum and g_{eff} the effective g value of the $J=\frac{1}{2}$ state. If g_{eff} is a measure for the spin splitting of the shallow bound electron, it is expected to be the same as the conduction-band value g_e.

The final state of the transition is a $J=\frac{3}{2}$ state (or Γ_8 state), and it is caused by the bound hole. The most general linear Zeeman Hamiltonian of such a bound hole is[14]

$$\mathcal{H}=K\mu_B\vec{J}\cdot\vec{H}+L\mu_B(H_xJ_x^3+H_yJ_y^3+H_zJ_z^3)\,, \tag{2}$$

where $\vec{J}$ is the total angular momentum and K and L are the isotropic and anisotropic g values of the bound hole, respectively. Let us first assume that anisotropy is negligible. We therefore use only the isotropic part of Eq. (2). The polarizations of the different transitions in Fig. 5 are indicated by $\parallel$, which means $\vec{E}\parallel\vec{H}$, RCP and LCP. The numbers 1–6 label the different transitions. From a comparison of Fig. 5 with our experimental pattern, we derive directly the values of g_{eff} and K according to Eqs. (1) and (2). Neglecting L, we get

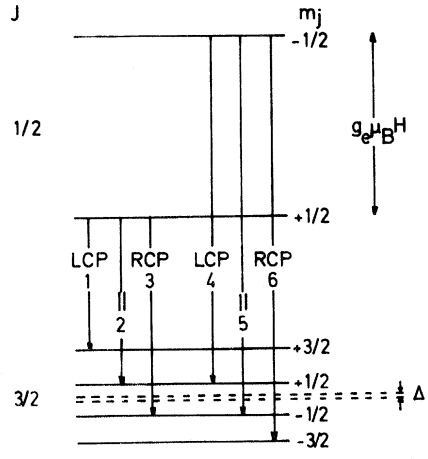

FIG. 5. Splitting pattern of the decay of a (A^0, X) complex with $\Gamma_6(J=\frac{1}{2})$ symmetry of the ground state. The polarization of the different transitions is as indicated. The observable oscillator-strength ratios of the different components are $I_1:I_2:I_3=3:4:1$ and $I_4:I_5:I_6=1:4:3$.

$$\Omega_{61} = |(h\omega_6 - h\omega_1)| = (|g_{\text{eff}}| + 3|K|)\mu_B H , \quad (3)$$

$$\Omega_{52} = |(h\omega_5 - h\omega_2)| = (|g_{\text{eff}}| + |K|)\mu_B H . \quad (4)$$

These energy differences were chosen because the different shifts of the centers of gravity of the $|m_j| = \frac{1}{2}$ and $|m_j| = \frac{3}{2}$ hole states are eliminated in this case.

We now verify the assumption $L \simeq 0$ made in Eqs. (3) and (4). Subtracting Eq. (4) from Eq. (3) we get for a magnetic field $\vec{H} \parallel [100]$

$$\Omega_{61} - \Omega_{52} = (2K + \tfrac{13}{2} L)\mu_B H , \quad (5)$$

without neglecting L. Combining a set of other components, we get the following combination of K and L:

$$\tfrac{1}{2}(\Omega_{31} - \Omega_{64}) = \tfrac{1}{2}[(h\omega_3 - h\omega_1) + (h\omega_6 - h\omega_4)] = (2K + \tfrac{7}{2} L)\mu_B H . \quad (6)$$

Substracting Eq. (5) from Eq. (6), we get

$$\tfrac{1}{2}(\Omega_{31} - \Omega_{64}) - (\Omega_{61} - \Omega_{52}) = 3L\mu_B H , \quad (7)$$

which was found within the experimental error to be zero for the BE_1, BE_2, and BE_4 lines (or at least L should be smaller than 0.03). Therefore the assumption $L \simeq 0$ proved to be justified. As example the variation of the energy difference with magnetic field, as given in Eqs. (3) and (4), are depicted in Fig. 6 for line BE_2. The resulting K value is $K_2 = 0.19 \pm 0.03$. The different K values we were able to determine are summarized in the last row of Table II, together with the localization energies E_B of the excitons to the neutral acceptors.

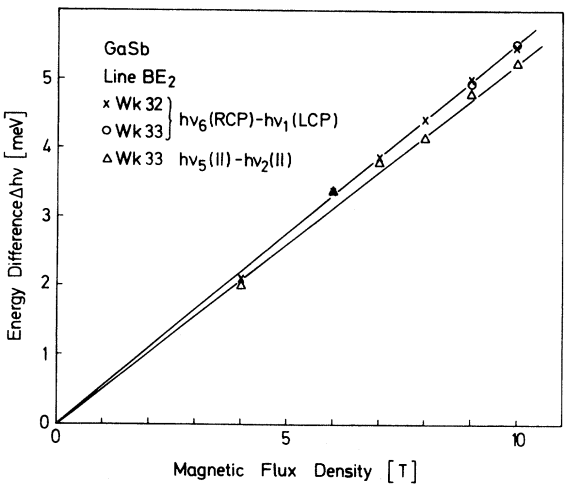

FIG. 6 Energy differences between the high-energy ($BE_2\uparrow$) RCP and the low-energy ($BE_2\uparrow$) LCP components (crosses and circles) and between the two components in $\vec{E} \parallel \vec{H}$ polarization (triangles) of the line BE_2. The most exact values are those at the highest fields (8, 9, and 10 T): The straight lines are drawn considering only these points. The difference ΔE between the two lines in $2K\mu_B H$ (see text).

They differ slightly from complex to complex: K increases with increasing localization energy E_B. This *relative* effect is an unambiguous experimental observation (K_4 is always $> K_2 > K_1$), as is shown in Fig. 3 for K_1 and K_2. There the low-energy ↑ components are drawn in such a way that the RCP components of BE_1 and BE_2 are at the same energetic position. The energy difference between the two circularly polarized components of BE_1 and BE_2 in this figure is equal to 2 K (neglecting L and Δ). It can clearly be seen here, that 2 K (BE_2) > 2 K (BE_1). The errors given in Table II have only the meaning of errors of the *absolute* values. The increase of K with increasing E_B is an unexpected result, if we assume that $E_B \propto E_A$ according to Haynes's rule[9]: the g factor should be reduced if the binding center becomes deeper[30]; a possible explanation is given in Sec. IV D.

The value for $K_4 = 0.3 \pm 0.05$ given in Ref. 6 agrees with our value only very roughly. The determination of the K value in Ref. 6 is very indirect: oscillator strengths (which are partially not correct[17]) are used to extract from old published absorption data[18,19] the K value. So the present data are the first direct and reliable determination of the K value of bound excitons in GaSb, although the absolute error is still about 20%.

The bound electron g value is $g_{\text{eff}} = -8.95 \pm 0.15$ and is the same for the three complexes BE_1, BE_2, and BE_4. This g value agrees within the limit of error exactly with the conduction-band g_e value that we recently determined to be $g_e = -9.1 \pm 0.2$.[13] It should be mentioned that our $|g_{\text{eff}}|$ is larger than the value determined recently by magnetopiezo-reflection[20] ($g_e = -7.8 \pm 0.8$) and magnetophotoconductivity[21] ($g_e = -8.4 \pm 0.8$). This disagreement might be due to the fact that excitonic effects for the lower Landau levels and effects of the nonparabolicity of the higher Landau levels were neglected in Refs. 20 and 21. The negative sign of g_{eff} and the positive sign of K could be unambiguously identified from the sequence of the different polarized components, as given in Fig. 5.

C. Diamagnetic effects

The problem of an exciton bound to a deep acceptor resembles in a first approximation that of a neutral donor, concerning diamagnetic effects. In this picture two holes are tightly bound to the acceptor and an electron is trapped by the Coulomb field of the virtual "A^+ complex." The binding of the electron should not be very tight, due to the small effective mass of the electron in GaSb [$m_e^* = 0.0405 m_0$ (Ref. 13)]. This simple description is supported by the results of the temperature dependence of the intensity of different (A^0, X) lines in GaSb and GaAs: The first ionization step of a deep (A^0, X) complex is always approximately the donor

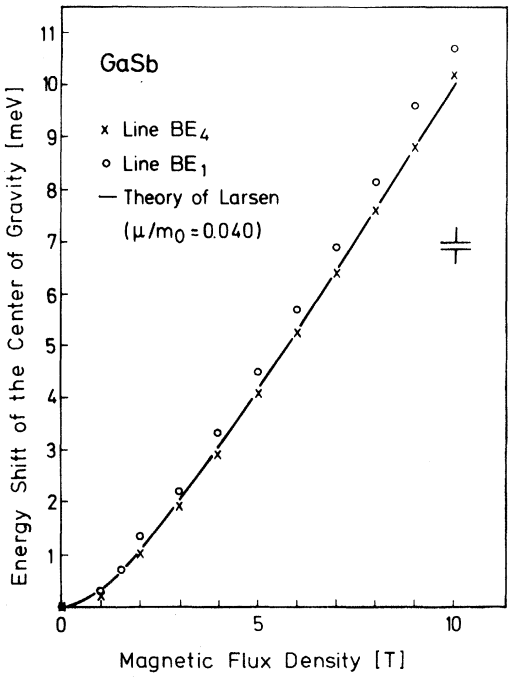

FIG. 7. Energy shift of the center of gravity of the two components ↑ and ↓ vs magnetic field. The crosses refer to line BE_4, the circles to line BE_1. The solid line is a fit to the crosses (line BE_4) according to the theory of Larsen (Ref. 23) and Cabib *et al.* (Ref. 24).

binding energy.[12,22]

Larsen[23] calculated the variation of the binding energy E_D of a hydrogenic donor in a magnetic field. His computation was further improved by Cabib *et al.*,[24] who presented variational calculations for $E_D(H)$ also for the intermediate field region, where $E_D(H=0) \leq \frac{1}{2}\hbar\omega_c$.

In Fig. 7 we show the magnetic field dependence of the center of gravity of the various Zeeman components of the deepest bound exciton BE_4 and one exciton with smaller localization energy (BE_1). This shift is quite different from that of a free electron to acceptor transition (for this transition see Refs. 13 and 25). A fit was made for the BE_4 line with the theory of Cabib *et al.*[24] using μ_0/m_0 as a free parameter. The best fit was obtained with a mass $\mu_0 = 0.040 m_0$, a value which is, in fact, very close to the free-electron value $m_e^* = 0.0405 m_0$.[13]

The solid line in Fig. 7 was calculated with this value. In the complex BE_1, the exciton is somewhat weaker bound to the neutral acceptor. Thus we expect a larger diamagnetic shift in this case, due to the fact that the holes involved in the complex are less tightly bound. This behavior is reflected by Fig. 7 exactly. These results confirm the validity of the simple picture of an A^+ complex binding an electron and are in qualitative agreement with some experimental results recently obtained for deep (A^0, X) complexes in GaAs.[26–28] It must be mentioned here that the experimental results in Ref. 26 are misinterpreted: The theory advanced there consists of separating the bound exciton into the free-exciton problem and an effective binding potential of the impurity. This separation ansatz is *not* applicable for the case of deep lying (A^0, X) complexes because the excitonic hole is stronger bound to the acceptor than to the excitonic electron. In our case the problem reduces to that of a donor in a magnetic field, as stated above.

In Sec. IV C we already mentioned that a different diamagnetic shift is found for different $|m_j|$ components of the final state. More precisely, the lines 1 and 6 or the lines 2, 3, 4, and 5 show the same shift (see Fig. 5). This different shift of these two groups of lines can be only due to a different diamagnetic shift of the $|m_j| = \frac{1}{2}$ and $\frac{3}{2}$ acceptor states. An analogous "diamagnetic splitting" was recently reported for the first time for the exciton bound to the deep acceptor tin in GaAs.[28] This splitting was predicted theoretically on the basis of a perturbation calculation of an acceptor in a magnetic field, taking into account the complete Hamiltonian of the valence band. An analogous diamagnetic splitting was recently predicted for free excitons.[29]

The diamagnetic splitting Δ is directly proportional to a_0^2,

$$\Delta = (eH/c)^2 (a_0^2/2\mu_0)\alpha_2 \,. \tag{8}$$

a_0 is the radius of the ground-state wave function of the acceptor, $\alpha_2 = 0.61$ for $\vec{H} \parallel [100]$, and $\mu_0 = m_0/\gamma_1$ (γ_1 is the Luttinger parameter). In the derivation of this expression, no other important assumption was made than that of a spherical symmetry of the binding Coulomb potential. Though the theory[8] was derived for an effective-mass acceptor, one can conclude that the (A^0, X) decay involving the deeper acceptor should show a smaller diamagnetic splitting. However, line BE_1 shows a smaller diamagnetic splitting than line BE_2.

D. Depth of the binding acceptors and Haynes's rule

Haynes's rule postulates an increase of E_B with increasing binding energy of the acceptor. The increasing binding energy E_B of the bound excitons BE_1 to BE_4 could be used in this connection for a tentative assignment of the bound exciton to the acceptors reported in Refs. 11 and 25. But this approach immediately leads to two severe contradictions: The isotropic g value K of a bound hole is expected to become smaller with increasing binding energy.[30] The diamagnetic splitting is proportional to a_0^2. In fact, we found $K(BE_1) < K(BE_2) < K(BE_4)$ and $\Delta(BE_1) < \Delta(BE_2)$ (see Table II). The sequence of the K values agrees with the sequence

of the Δ values. Both implicate that the acceptor binding energy does not increase but decrease in the sequence $BE_1 \ldots BE_2$, which means that Haynes's rule does not hold for these centers. On the other hand this is *not* the first time that deviations from this rule are demonstrated. For a series of acceptors in InP,[31] it was found that the binding energy of the acceptor does not increase with the localization energy of the exciton. If we compare the excitons bound to the neutral copper C acceptor[5] and to neutral tin[3,4] in GaAs, we find the same. The exciton bound to the copper C acceptor has the larger localization energy (13.5 meV relative to 8.1 meV) although it is the shallower acceptor ($\simeq$156 meV relative to 170 meV). We propose the BE_1 and BE_2 bound excitons in GaSb to be new examples that Haynes's rule is violated.

Concluding this short discussion of Haynes's rule, it should be pointed out that a violation of this rule over the whole range of binding energy of all four bound-exciton lines BE_{1-4} (an inverse relationship from 4.5 to 13.8 meV) would be much larger to previously observed forms[31,32] and reveals an entirely new situation. Most of the deviations which occur in GaP and Si were reasonably explained by Dean[32] with a modification of the original rule. His explanation could also hold for the deviations in GaAs and InP but not for BE_{1-4} in GaSb. An unambiguous conclusion that the rule is violated for all four bound excitons is, unfortunately, not possible, because we have no reliable values of Δ and K for BE_3 and of Δ for BE_4; further, our evidence is based on a relatively indirect argument but not on the direct and independent knowledge of E_B *and* E_A.

An effective assignment of the BE lines to appropriate acceptors could be achieved by an independent determination of the K values of the different acceptors from free-electron to neutral-acceptor transitions.

V. SUMMARY

The linear and quadratic Zeeman effect of four different recombination lines at 805.4, 803.4, 800.1, and 796.1 meV in GaSb was investigated. Excitons bound to neutral acceptors were found to be responsible for at least three of the lines. An energy state with $J_{tot} = \frac{1}{2}$ is proved to be the lowest of the four investigated (A^0, X) complexes.

From a numerical analysis of the Zeeman pattern for the first time isotropic bound hole g values K could be derived for different neutral acceptors in GaSb. A verification of the very recent theoretical prediction of a diamagnetic splitting of acceptor states is presented. The diamagnetic shift of a deep (A^0, X) state was successfully fitted by means of Larsen's theory of a donor in a magnetic field, under the assumption that there is an analogy between an acceptor binding two holes (A^+) and an ionized donor (D^+).

One surprising result, however, is that both K value and difference Δ between the diamagnetic shifts of the $|m_j| = \frac{1}{2}$ and $|m_j| = \frac{3}{2}$ hole states *increase* with *increasing* localization energy of the exciton. Therefore Haynes's rule, which states that the exciton binding energy is proportional to the ionization energy of the neutral binding center, might not be valid either in the case of the excitons investigated here.

VI. ACKNOWLEDGMENTS

We are indebted to K. Cho, W. Kottler, and T. N. Morgan for many helpful discussions. Thanks are due to K. Dransfeld, M. H. Pilkuhn, and H. J. Queisser for their interest in the work, and to P. J. Dean and A. M. White for a critical reading of the manuscript. The experimental assistance of H. Krath is gratefully acknowledged. The crystals were kindly supplied by W. Jakowetz and C. Wölk. One of us (W. R.) is very grateful for the hospitality of the Hochfeld-Magnetlabor in Grenoble.

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†Work supported by the Stiftung Volkswagenwerk and the Deutsche Forschungsgemeinschaft (SFB 67).

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