Magnetic-Field-Induced Energy Shifts of the Ground State of Bound Excitons in GaAs

F. Willmann, W. Dreybrodt, and M. Bettini
Max-Planck-Institut für Festkörperforschung, Stuttgart, West Germany
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We present photoluminescence measurements on bound excitons in Sn- and Cu-doped epitaxial GaAs in magnetic fields up to 12 T. The bound-exciton lines split; the shift towards higher energies of the center of gravity is identical for both dopants, despite their largely differing binding energies. The magnitude of the shift is comparable to that of the free exciton. A theoretical explanation assuming a short-range exciton-acceptor interaction potential accounts for the observed data. The experimental data are fitted by Larsen's theory of the hydrogenic problem. The excitonic mass obtained from this fit is close to the reduced mass of the electron and the heavy hole. This seems to be a general result, confirmed by reconsideration of older experimental data on free and bound excitons in GaSb, InSb, and Ge with the most recent band parameters.

I. INTRODUCTION

The behavior of the ground-state energy of free excitons in a magnetic field is theoretically well described by a variational calculation in both the high-field and low-field region.[1-3] In the case of shallow effective-mass donors this theory is well established experimentally.[4,5] Most of the work done on excitons, however, deals mainly with Zeeman-effect splittings and investigates shifts of the ground-state energy only in the diamagnetic range. Measurements of the diamagnetic shift in CdS[6] and GaSb[7] revealed that the magnitudes of the shifts of free and bound excitons are approximately equal.

In order to obtain more experimental information on the exciton in magnetic fields, it is necessary to extend the measurements to high field, where $\gamma = \hbar\omega_c/2R > 1$, i.e., the ratio of the cyclotron resonance energy of the exciton mass to twice the binding energy of the exciton.

In this work we report photoluminescence measurements of the magnetic shift of several excitons bound to neutral acceptors in Cu- and Sn-doped epitaxial GaAs[8,9] up to fields of 12 T, i.e., $\gamma = 2$. Our results show that within the experimental error the magnetic shift of all these bound excitons, which differ widely in their binding energy to the acceptors, are identical. They seem, however, to be slightly larger than the magnetic field shift of the free-exciton ground-state energy, which has been measured in absorption.[10]

A theoretical explanation based on Larsen's[2] variational approach is given, which is applied to the Hamiltonian of the exciton bound by a short-range potential[11,12] to the neutral acceptor. From this treatment we conclude that the magnetic shift of the ground-state energy results only from the internal motion of the excitonic subsystem. The shift is independent of the binding energy to the neutral-acceptor subsystem and should be that of a free exciton. We were able to fit the experimental data by using Larsen's results.[2] This fit was done by using the excitonic mass as fitting parameter. The mass obtained is close to the electron-heavy-hole reduced mass in contrast to $\vec{k}\cdot\vec{p}$ calculations[13,14] where one obtains a reduced mass in zero magnetic field determined by the electron mass and the "isotropic valence-band mass" $1/\gamma_1$. This is a puzzling result, which is also true, however, in other materials such as GaSb,[7] InSb,[15] and Ge[16] and up to now has not been noticed.

II. EXPERIMENTAL

The photoluminescence spectra were obtained from liquid-phase-epitaxial GaAs crystals slightly doped with Sn or Cu. The preparation technique and the electrical properties have been described previously.[9,18] The samples were immersed in liquid He at the center of a 12.6-T Nb_3Sn magnet. The aperture of the system was $f/5$. Spectra were taken in the Faraday configuration with normally incident excitation by the 514.5-nm line of an Ar^+ laser. The luminescent radiation was detected by using a $\frac{3}{4}$-m Spex grating monochromator and a photomultiplier (FW 118) cooled by dry nitrogen gas. The exciting laser radiation was chopped at about 700 Hz and the luminescent signal was detected by conventional lock-in techniques.

III. EXPERIMENTAL RESULTS

We have measured the magnetic shift of the emission line near 1.507 eV in Sn-doped GaAs, which has been previously identified as a recombination of an exciton state bound to a neutral Sn acceptor.[8,17] The binding energy of the neutral acceptor is about 170 meV,[18] while the exciton-acceptor binding energy is 8 meV.[17]

Figure 1 shows the bound-exciton emission line and its behavior in a magnetic field, measured in the Faraday configuration. As has been shown recently[8,17] the recombination line exhibits a linear Zeeman splitting due to the spin splitting of the

excitonic motion and the splitting of the acceptor ground state. In the Faraday configuration only lines with selection rule $\Delta m_j = \pm 1$ are seen. The magnetic shift of the ground-state energy is determined from the center of gravity of the two outermost lines.[8]

This magnetic shift is shown in Fig. 2. The triangles represent the shift of the center of gravity of the recombination line of the exciton bound to the Sn acceptor. The same experiment has been performed on the bound-exciton spectrum in GaAs:Cu. In this case two excitons bound to different Cu-complex centers are observed and their electronic structure has been identified by measurements of their Zeeman splitting.[9] The energies of these two lines are at 1.5026 and 1.4832 eV corresponding to a binding energy of the excitons to the neutral acceptor of 12.6 and 31.9 meV, respectively. The magnetic shift of the center of gravity of their Zeeman patterns are represented by the full and open circles in Fig. 2. It is remarkable that all three differently bound excitons exhibit an identical behavior in spite of their largely differing binding energies. Furthermore, the shifts are comparable to the shift of the free exciton as measured in absorption.[10] This is shown by the squares in Fig. 2. The shift of the bound excitons up to 3.0 T is proportional to B^2, thus representing the diamagnetism of the complex. The observed diamagnetic shift rate for all bound-exciton lines is 6.1×10^{-2} meV T^{-2} in agreement with the value of White *et al.*[8] for the Sn bound exciton.

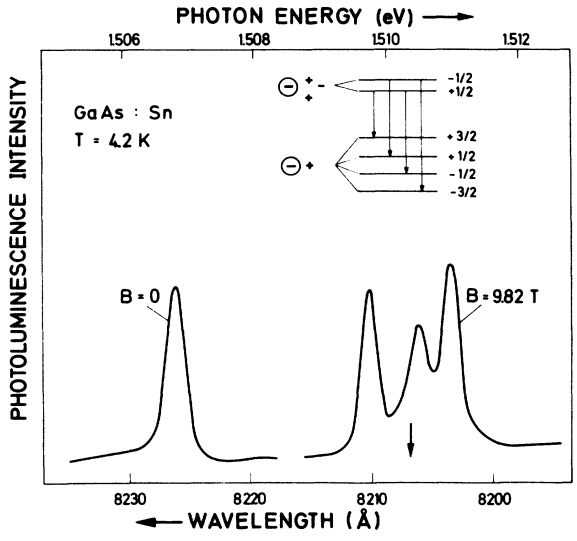

FIG. 1. Photoluminescence spectra of the bound-exciton line measured in the Faraday configuration. The Zeeman pattern is due to the splitting as shown by the term scheme. The arrow represents the center of gravity used to determine the ground-state energy shift.

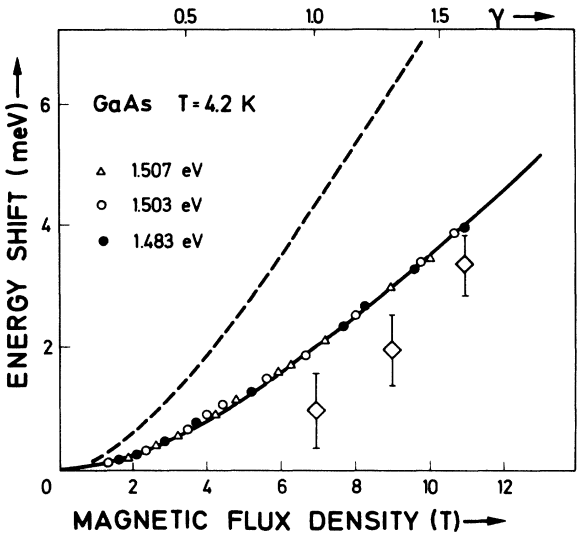

FIG. 2. Shift of the center of gravity for excitons bound to Sn (△) and Cu acceptors (●, ○). The solid line through the experimental points is calculated by Larsen's theory. The γ scale corresponds to the calculated mass $\mu_{expt} = 0.068\ m_e$. The dashed line represents the calculated magnetic shift of an exciton with $\mu_0 = 0.044\ m_e$. ◇ represents the magnetic shift of the free exciton measured in absorption after Ref. 10.

IV. THEORETICAL

In order to provide a theoretical basis for understanding the above results, we start with the Hamiltonian of the bound exciton without magnetic field

$$H = H_{FE} + H_A + V(\vec{r}_e, \vec{r}_h, \vec{r}_{hA}, \vec{r}_A) \ , \tag{1}$$

where H_{FE} is the Hamiltonian of a free exciton and H_A is the Hamiltonian of the neutral acceptor. The interaction potential between these two complexes is $V(\vec{r}_e, \vec{r}_h, \vec{r}_{hA}, \vec{r}_A)$, $\vec{r}_e$ and $\vec{r}_h$ are the position coordinates of the electron and the hole representing the free exciton. $\vec{r}_{hA}$ is the position coordinate of the hole bound to the acceptor, and $\vec{r}_A$ is the position of the impurity. Because of the large mass of the ion terms in $\vec{r}_A$ do not need to be considered further. After transformation into center-of-mass and relative coordinates for both the free exciton, i.e., $\vec{\rho}_{ex}$ and $\vec{R}_{ex}$, and the acceptor subsystem, i.e., $\vec{\rho}_A$ and $\vec{R}_A$, we obtain

$$H_{FE} = -\frac{\hbar^2}{2M_{ex}} \nabla^2_{R_{ex}} - \frac{\hbar^2}{2\mu_{ex}} \nabla^2_{\rho_{ex}} - \frac{e^2}{\epsilon \rho_{ex}} \ , \tag{2a}$$

$$H_A = -\frac{\hbar^2}{2m_h^*} \nabla^2_{\rho_A} - \frac{e^2}{\epsilon \rho_A} \ , \tag{2b}$$

$$V(\vec{r}_e, \vec{r}_h, \vec{r}_{hA}, \vec{r}_A) = V(\vec{R}_A, \vec{\rho}_A, \vec{\rho}_{ex}, \vec{R}_{ex}) \ . \tag{2c}$$

M_{ex} and μ_{ex} are the total and reduced masses of the exciton subsystem, respectively, m_h^* is the hole mass, and ϵ is the dielectric constant.

We solve Eq. (1) with the *Ansatz* used by Ref. 11 which was experimentally justified in CdS.[12] To do so, we replace the interaction potential $V(\vec{\rho}_A, \vec{R}_{ex}, \vec{\rho}_{ex})$ by a short-range potential $V_{eff}(\vec{R}_{ex})$ which acts only on the excitonic center-of-mass coordinate. Thus, the problem is easily separated by using a wave function

$$\Psi = \phi_A(\vec{\rho}_A)\,\phi(\vec{\rho}_{ex}) f(\vec{R}_{ex}), \tag{3}$$

where $\phi(\vec{\rho}_{ex})$ is the internal motion of the free exciton, $\phi_A(\vec{\rho}_A)$ is the envelope function of the neutral acceptor, $f(\vec{R}_{ex})$ is the eigenfunction of the center-of-mass motion of the exciton around the acceptor, i.e., the solution of

$$H_{R_{ex}} f(\vec{R}_{ex}) = \left(-\frac{\hbar^2}{2M_{ex}}\nabla^2_{R_{ex}} - V_{eff}(\vec{R}_{ex})\right) \times f(\vec{R}_{ex}) = E_B f(\vec{R}_{ex}). \tag{4}$$

By replacing $V_{eff}(\vec{R}_{ex})$ by a δ function and adjusting $f(\vec{R}_{ex})$ for the observed binding energy E_B of the exciton to the acceptor[11] we get

$$f(\vec{R}_{ex}) = e^{-R_{ex}/\lambda}/(2\pi\lambda)^{1/2} R_{ex}, \qquad \lambda = \hbar^2/(2M_{ex}E_B)^{1/2}. \tag{5}$$

In the presence of a magnetic field one has to add to the Hamiltonian of Eq. (1) a term H_m:

$$H_m = \left(+\frac{ie\hbar}{m_e^* c}\vec{A}(\vec{r}_e)\vec{\nabla}_{r_e} - \frac{ie\hbar}{m_h^* c}\vec{A}(\vec{r}_h)\vec{\nabla}_{r_h} + \frac{e^2}{2m_e^* c^2}A^2(\vec{r}_e) + \frac{e^2}{2m_h^* c^2}A^2(\vec{r}_h)\right) + \left(-\frac{ie\hbar}{m_h^* c}\vec{A}(\vec{r}_{hA})\vec{\nabla}_{r_{hA}} + \frac{e^2}{2m_h^* c^2}A^2(\vec{r}_{hA})\right). \tag{6}$$

The vector potential $\vec{A}$ is defined in the symmetric gauge $\vec{A}(\vec{r}) = \frac{1}{2}(\vec{H}\times\vec{r})$. The first large parentheses contain the magnetic part of the free-exciton Hamiltonian, the second contain the magnetic part of the acceptor Hamiltonian.

In analogy to the treatment without magnetic field and using for the excitonic motion the eigenfunction

$$\phi_{ex} = \exp\left[\left(\frac{-ie\vec{A}(\vec{\rho}_{ex})}{\hbar c}\right)\vec{R}_{ex}\right] \times \phi(\vec{\rho}_{ex})\sum_{\vec{k}} a(\vec{k}) e^{i\vec{k}\cdot\vec{R}_{ex}}, \tag{7}$$

where $a(\vec{k})$ is the Fourier transform of $f(\vec{R}_{ex})$, we obtain the following Schrödinger equation for the excitonic subsystem:

$$\left[-\frac{\hbar^2}{2\mu_{ex}}\nabla^2_{\rho_{ex}} - \frac{e^2}{\epsilon\rho_{ex}} + \frac{ie\hbar}{c}\left(\frac{1}{m_e^*} - \frac{1}{m_h^*}\right)\vec{A}(\vec{\rho}_{ex})\vec{\nabla}_{\rho_{ex}} + \frac{e^2}{2\mu_{ex}c^2}A^2(\rho_{ex})\right]\phi_{ex} - \left(\frac{2e\hbar}{M_{ex}}\vec{A}(\vec{\rho}_{ex})\cdot\sum_{\vec{k}}\vec{k}a(\vec{k})e^{i\vec{k}\cdot\vec{R}_{ex}} + \frac{\hbar^2}{2M_{ex}}\sum k^2 a_k e^{i\vec{k}\cdot\vec{R}_{ex}}\right)\phi(\vec{\rho}_{ex})\exp\left(-\frac{ie\vec{A}(\vec{\rho}_{ex})\vec{R}_{ex}}{\hbar c}\right) = E\phi_{ex} + V_{eff}(\vec{R}_{ex})\phi_{ex}. \tag{8}$$

Since we are not interested in the Zeeman effect of the problem we dispose of the Zeeman terms $\vec{A}(\vec{\rho}_{ex})\cdot\vec{\nabla}_{\rho_{ex}}$. The Hamiltonian (8) can be written

$$H = \sum_{\vec{k}} a_k H_k, \tag{9}$$

where H_k is the Hamiltonian of an entirely free exciton.[19] The eigenenergy E is then given by

$$E = \sum_k a_k E_k. \tag{10}$$

Using Eq. (9) and Eq. (10) and treating the term which is linear in $\vec{k}$ and $\vec{A}(\vec{\rho}_{ex})$ as a perturbation, it can be easily shown that this term contributes nothing in first order to the ground-state energy of Eq. (8).

Now we can separate Eq. (8) into completely decoupled Schrödinger equations of the internal free-exciton motion of excitons with $\vec{k}=0$ and the center-of-mass motion;

$$\left(-\frac{\hbar^2}{2\mu_{ex}}\nabla^2_{\rho_{ex}} - \frac{e^2}{\epsilon\rho_{ex}} + \frac{e^2}{2\mu_{ex}c^2}A^2(\vec{\rho}_{ex})\right) \times \phi(\vec{\rho}_{ex}) = E_{ex}\phi(\vec{\rho}_{ex}), \tag{11}$$

$$\left(-\frac{\hbar^2}{2M_{ex}}\nabla^2_{R_{ex}} + V_{eff}(\vec{R}_{ex})\right) f(\vec{R}_{ex}) = E_B f(\vec{R}_{ex}). \tag{12}$$

Since we have replaced $V(\vec{r}_e, \vec{r}_h, \vec{r}_{hA})$ by $V_{eff}(\vec{R}_{ex})$ and because of Eq. (3), the acceptor is completely decoupled. Its Schrödinger equation after neglecting Zeeman terms is

$$\left(-\frac{\hbar^2}{2m_h^*}\nabla^2_{\rho_A} - V(\vec{\rho}_A) + \frac{e^2}{2m_h^* c^2}A^2(\vec{\rho}_A)\right) \times \phi_A(\vec{\rho}_A) = E_A\,\phi_A(\vec{\rho}_A). \tag{13}$$

The results of this model are summarized as follows: (a) The magnetic field dependence of the ground-state energy of the bound exciton is just the sum of the energy shift of a free exciton and an isolated neutral acceptor. (b) The exciton-to-acceptor binding energy is entirely unaffected by a magnetic field. (c) Since the final state in the recombination process is the neutral-isolated-acceptor ground state, the experimentally observed energy shift is only due to the change of the exciton energy of Eq. (11). This result explains our data, and the expected behavior had already been ob-

served experimentally in GaSb[7] and CdS[6] but had not been discussed further.

V. DISCUSSION

In order to compare with our experimental results we calculate the diamagnetic shift of the exciton in the effective-mass approximation. In the case of a ground-state 1s function the diamagnetic energy is given with perturbation theory by

$$\Delta\epsilon(B) = e^2B^2a_0^2/4\mu_{ex}c^2, \tag{14}$$

where a_0 is the effective Bohr radius and μ_{ex} the mass of the hydrogenic problem, i.e., the exciton radius and reduced mass, respectively.

From the measured diamagnetism of 6.1×10^{-2} meV T^{-2} we calculate the experimental exciton effective mass as $\mu_{expt} = 0.068m_e$. At higher magnetic fields above the 3 T the energy of the exciton problem is given by Larsen's theory.[2] Using the mass obtained from the diamagnetism and the theoretical data[3] we obtain the full line through the experimental points in Fig. 2. The agreement is excellent and to our knowledge is obtained experimentally for the first time in the intermediate-field region, i.e., $\gamma \approx 1$. The mass, however, which has been used to fit the experimental data is far from the reduced mass $\mu_0 = 0.044\ m_e$, which has been calculated by $\vec{k}\cdot\vec{p}$ theory in a three-band model.[13,14] The $\vec{k}\cdot\vec{p}$ reduced mass accounts well for the thus calculated and measured[20] energies of the exciton series without magnetic field. The magnetic shift, calculated with this mass is shown by the dashed line in Fig. 2 and is much larger than the observed one.

If one compares the experimental mass $\mu_{expt} = 0.068m_e$ to the reduced mass of an exciton consisting of an electron and a heavy hole, which is $\mu_{eh} = 0.060m_e$ one might conclude that in magnetic fields the excitonic mass is determined rather by the heavy hole than by the "isotropic valence-band mass." This result is puzzling. It is true, however, in GaSb,[6] InSb,[15] and Ge[16] as well. Table I compares the masses calculated from the experimentally observed diamagnetic shift of bound or free excitons in these materials to the mass calculated from the $\vec{k}\cdot\vec{p}$ theory of the exciton[13] with the band parameters of Lawaetz.[14] The agreement between the last two columns indicates that the magnetic behavior of excitons is generally governed by the heavy-hole and not the isotropic-hole mass.

It should be noted that the basis of our theoretical approach is to separate the interaction potential $V(\vec{\rho}_A, \vec{\rho}_{ex}, \vec{R}_{ex})$ into the sum $V(\vec{\rho}_A) + V(\vec{\rho}_{ex}) + V(\vec{R}_{ex})$. In this case the separation into an isolated-acceptor and free-exciton Hamiltonian is always possible. So far we have neglected the influence of the interaction potential on the internal motion of both the acceptor and the exciton. This approximation is valid for $E_B \ll E_{ex}$. In this case the exciton moves as a quasiparticle at a large distance R_{ex} from the impurity, where R_{ex} exceeds the radius ρ_{ex} of the internal motion.

TABLE I. Reduced masses of the free exciton as calculated by $\vec{k}\cdot\vec{p}$ theory μ_0, as measured by magnetic shift μ_{expt}, and as calculated from electron and heavy-hole mass μ_{eh}. The masses are given in units of the free-electron mass m_e.

Material	Type of exciton	μ_0[a]	μ_{expt}	μ_{eh}[a]
Ge	free	0.025	0.036[b]	0.034
InSb	free	0.009	0.0136[c]	0.0136
GaSb	free and bound	0.029	0.043[d]	0.041
GaAs	bound	0.044	0.068	0.060

[a] Reference 14.
[b] Reference 16.
[c] Reference 15.
[d] Reference 7.

In the other limiting case where $E_B \gg E_{ex}$ and $m_h^* \gg m_e^*$, the expectation value of R_{ex} is, according to Eq. (5), much smaller than that of ρ_{ex}. Since $m_e^* \gg m_h^*$, the expectation value of R_{ex} is, according purity ion, whereas the electron on the average is at a large distance and the electron sees mainly the potential of an ionized impurity. Hence, the excitonic part of the problem reduces to that of a hydrogenic donor. Thus, within these two limiting cases our theoretical explanation holds reasonably well, if one takes into account that the effective mass of the exciton system has to be changed slightly between the effective electron mass and the effective electron–heavy-hole reduced mass.

In fact in the bound excitons we observe a mass of $0.068m_e$ which is very near to the electron effective mass of $0.067m_e$.[14] The expectation values of R_{ex} and ρ_{ex} are about 30 and 140 Å, respectively, for $E_B = 8$ meV. This seems to be near to the second limiting case. For further clarification of the problem it is necessary to measure exactly the free-exciton shift and the exciton bound to a shallow donor. Both these systems are in the low-binding limit and might exhibit smaller masses from their energy shift.[21]

VI. CONCLUSIONS

We have measured the magnetic field dependence of the ground-state energies of excitons bound to different acceptors in Sn- and Cu-doped epitaxial GaAs in magnetic fields up to 12 T. The magnetic shift of these differently bound excitons is identical, though the binding energies differ widely.

This behavior is explained theoretically by separating the bound-excitonic complex into the two subsystems: the excitonic part, which is bound only by its center-of-mass motion to the acceptor, and the isolated neutral impurity. As a result the bind-

ing energy of the exciton to the impurity is independent of the magnetic field and the magnetic shift is the sum of both subsystems. Experimentally, only the magnetic shift of a free exciton contributes. The experimental data can be fitted accurately by using Larsen's theory of the hydrogen problem in a magnetic field up to $\gamma \approx 2$. The mass thus obtained is closely related to a reduced mass of the electron and heavy hole. By revising older experimental data on magnetic shifts in Ge, InSb, and GaSb this seems to be generally valid for both free and bound excitons.

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