Magneto-optical Investigation of the Free-Exciton Reflectance from High-Purity Epitaxial GaAs

R. Dingle*
Research School of Physical Sciences, The Australian National University, Canberra, A.C.T. 2600, Australia
Bell Laboratories, Murray Hill, New Jersey 07974
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The free-exciton reflectance structure at 1.5149 ± 0.0001 eV (2 K, zero field) in GaAs has been studied with polarized light in magnetic fields up to $H \approx 250$ kG. Large shifts, up to six times the exciton binding energy, and complex splittings of the eightfold-degenerate exciton ground state have been observed. These effects have been analyzed with a simple hydrogenic model as well as with a low-field perturbation model that includes the anisotropy and degeneracy of the zinc-blende valence band at $k = 0$. The shifts are satisfactorily accounted for over the whole range, whereas only qualitative agreement between the predicted and observed splitting pattern is achieved. Reasons for this discrepancy are discussed.

I. INTRODUCTION

The importance of excitonic transitions in the understanding of band-edge absorption, reflection, and luminescence in elemental and compound semiconductors has now been properly recognized.[1-3] This awareness is due to activities in both experimental and theoretical spheres. From the experimental point of view, the availability of high-purity materials has allowed the direct observation of intense, resolved, sharp-line structure immediately below the energy of the band-to-band continuum in direct gap materials. In GaAs, for example, these structures have been associated[4-6] with exciton formation.

Most theoretical models consider the exciton in the hydrogenic approximation. In this case the exciton is composed of an electron and a hole which come from parabolic and nondegenerate energy bands. With such a model the binding energy of the exciton ground and excited states can be obtained, and the behavior of these quantities under external perturbations may be assessed. For example, a number of calculations of the free-exciton binding energy in the presence of an applied magnetic field have been made in the hydrogenic approximation.[7-13] Generally, these calculations give approximate agreement[2] with the available experimental data.[14]

Baldereschi and Lipari[15] have recently introduced a new theoretical approach for the investigation of the direct exciton in semiconductors with anisotropic and degenerate valence bands such as exist in the cubic diamond and zinc-blende structures. With their model, which is based upon the symmetry properties of the exciton effective-mass Hamiltonian, a correction to the hydrogenic zero-field exciton binding energy is obtained. This model appears to give good agreement[15] with data from a wide range of zinc-blende crystals.

The extension of this model to include small applied magnetic fields as a perturbation has been accomplished by Altarelli and Lipari (hereafter AL).[16] Small, but significant deviations from the behavior expected in the hydrogenic model are predicted. To date there is very little detailed low-field experimental data against which this theoretical model may be tested.[17]

In these laboratories we have been carrying out a detailed study of the direct free exciton in highly pure n-type vapor-phase-epitaxial layers of GaAs. Results of these luminescence, reflection, and absorption experiments at zero field and in the presence of uniaxial stress have already been reported.[5,6,18,19] From these data, a polariton model for the exciton has been proposed. The exciton ground-state binding energy has been established and some low-lying excited states have been observed. Details connected with line shapes and splittings have been analyzed.

In this paper the behavior of the exciton in low, intermediate, and large magnetic fields is reported. This behavior is compared against the predictions of the hydrogenic theories as well as against the AL low-field perturbation treatment. The principal results are: (i) The hydrogenic model gives a good over-all description of the ground-state energy of the GaAs free exciton over the range $\gamma \lesssim 8$ ($H = 0$–250 kG), where γ is the ratio of half the cyclotron resonance frequency divided by the effective rydberg R_0. At low fields sizable discrepancies, of the order of 20%, exist between theory and experiment. (ii) In the low-field limit, $\gamma < 0.4$, the AL model gives an improved fit to the ground-state energy. The combination of the best variational hydrogenic calculations of Cabib, Fabri, and Fiorio[12] with the corrections (to second-order perturbation theory) due to the valence-band complexity, as given by AL,[16] produces a rather good correspondence between experiment and theory for $\gamma < 0.4$. (iii) The qualitative nature

of the splitting pattern of the eightfold-degenerate exciton ground state in the magnetic field, i.e., the linear or Zeeman splitting, is correctly predicted by the AL model, although, with the currently available band parameters for GaAs,[20] we have not been able to obtain quantitative agreement between theory and experiment. At least part of this difficulty arises from the fact that for GaAs the band parameters are not known with sufficient accuracy from independent experiments.[21,22]

The paper is divided into four sections. Section II gives an outline of the experimental procedures. In Sec. III background information on the properties of a free direct exciton in a zinc-blende lattice, both with and without an externally applied magnetic field, is given. A comparison between theory and experiment in the presence of the external magnetic field is given in Sec. IV which is concluded by a short summary of our findings.

II. EXPERIMENTAL

Samples were n type, grown by vapor-phase epitaxy on GaAs substrates.[23] Total impurity concentrations were less than 10^{14} cm^{-3} and 77-K mobilities were in excess of 180 000 cm^2/V sec. Apart from normal cleaning activities no special surface preparation was undertaken. For all experiments the samples were immersed in pumped liquid helium or in helium exchange-gas atmosphere. Data were taken in both luminescence and reflection. The reflectance experiments were extended to higher fields than the luminescence and, in addition, the results are more precise. The free-exciton-luminescence results will not be considered in this paper.[24]

The low-magnetic-field data (to ~ 80 kG) were obtained with superconducting magnets at Bell Laboratories and at The Australian National University. Both Voigt and Faraday geometries, with linearly and circularly polarized light, were used. Results in fields above 100 kG (Faraday geometry) were obtained in the Magnet Laboratory of the Department of Engineering Physics at The Australian National University. Magnetic fields up to 300 kG are available at this facility. Spectra were recorded photographically and photoelectrically using a Jarrell-Ash 1 m Czerny-Turner spectrometer.

III. BACKGROUND INFORMATION

When a free exciton is formed at $k=0$ in a zinc-blende semiconductor a Γ_6 electron (T_d is the group of the wave vector at $k=0$) couples with a Γ_8 hole to produce $\Gamma_5+\Gamma_4+\Gamma_3$ exciton states. In the absence of electron-hole exchange and crystal-field effects these exciton states are degenerate. It has been shown elsewhere[18,19] that splittings due to these perturbations are small. At zero field the transition from the Γ_1 ground state of the crystal to the Γ_5 component of the exciton ground state is dipole allowed, whereas transitions to the Γ_4 and Γ_3 components are dipole forbidden. Certain external perturbations, such as a magnetic field, can mix the forbidden and Γ_5 allowed states so that field-induced intensity may appear in some of the forbidden transitions.

In the interpretation of the free-exciton reflectance spectrum given in this paper, we ignore the details of polariton behavior, spatial disperions, and other small perturbations and it is assumed that the exciton ground state is properly described by the degenerate $\Gamma_5+\Gamma_4+\Gamma_3$ set of states. The energy of these states is taken to be the minimum of the main reflectance feature, Fig. 1, which has been shown[18,19] to be very close to the energy of the transverse free exciton in our samples of GaAs.

In this brief survey no effort is made to reproduce the details of the various theoretical models that will be utilized in the succeeding sections; rather, an outline of the basic assumptions and a summary of the principal results will be given.

For a semiconductor with parabolic and nondegenerate conduction and valence bands the Wannier exciton Hamiltonian[25] can be reduced to that of the hydrogen atom and an exact description of the exciton energy spectrum (appropriately scaled by dielectric and mass parameters) and oscillator strengths is readily obtained. The inclusion of an external magnetic field into the model can also be accomplished with, in general, approximate solutions at the low- and high-field limits. The recent calculation, by Cabib, Fabri, and Fiorio[12] (CFF), covers the magnetic field range $0<\gamma<5$ (0–160 kG for GaAs) and is expected to

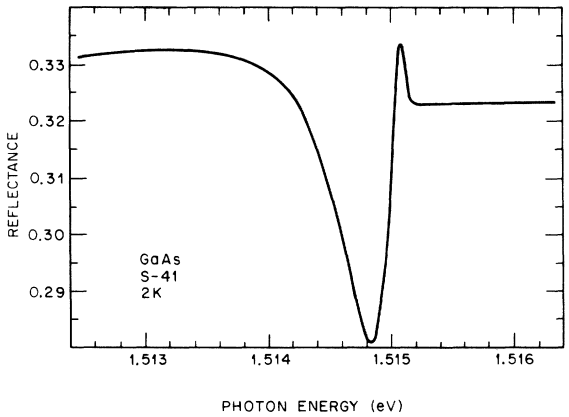

FIG. 1. A typical zero-field low-temperature exciton reflectance curve from high-purity GaAs. For the purposes of the present work the transverse exciton energy is taken to be at the minimum of the reflectance curve at 1.5149 ± 0.0001 eV.

TABLE I. Energy (effective rydbergs) of the ground state of the free exciton as a function of magnetic field γ ($\gamma = eH/2\mu_0 cR_0$). Taken from Ref. 12, but with values rounded to the third decimal place for comparison with experiment. The various entries are as given by Cabib, Fabri, and Fiorio (Ref. 12) and are taken from Refs. 7 (YKAv), 10 (PRv), 9 (Lv), 11 (BBv, BBa), and 12 (CFF) of this paper.

γ	YKAv	PRv	Lv	BBv	BBa	CFF
0.1	−0.844	−0.995		−0.995		−0.996
0.2	−0.839	−0.981		−0.981		−0.981
0.3	−0.811	−0.958	−0.96	−0.958		−0.958
0.4	−0.784	−0.929		−0.927		−0.929
0.5	−0.751	−0.894	−0.89	−0.890		−0.894
0.6	−0.713	−0.854		−0.849		−0.855
0.7	−0.670	−0.810	−0.81	−0.805		−0.811
0.8	−0.624	−0.762		−0.758		−0.764
0.9	−0.576	−0.712		−0.708		−0.715
1.0	−0.524	−0.659	−0.66	−0.655	−0.71	−0.662
1.5	−0.234	−0.364	−0.37		−0.37	−0.371
2.0	+0.092	−0.035	−0.04		−0.04	−0.044
2.5	+0.442	+0.317	0.31		0.31	0.305
3.0	+0.809	+0.686	0.68		0.67	0.671
4.0	+1.580	+1.458			1.45	1.438
5.0	+2.384	+2.265	2.25		2.24	2.239

give the most accurate values for the energy of an hydrogenic exciton in an external magnetic field. An incomplete summary of the results of the available hydrogenic calculations is given in Table I. In this paper we will compare our experimental data against the CFF predictions given in Table I.

Elliott and Loudon[8] have summarized their expectations of the hydrogenic exciton of a semiconductor in a large magnetic field in the following way. The exciton lines, and particularly the lowest one, should increase in intensity more rapidly than the magnetic field and should move to lower energies, relative to the absorption edge, but to higher energies on an absolute scale with increasing field (see Fig. 2). Thus the effect of a Coulomb field (i.e., of exciton formation) is to remove absorption intensity from the band edge and to concentrate this more and more in the lowest exciton line as the field increases. In the limit of infinite field, the lowest exciton line has infinite intensity and infinite binding energy.

We are able to make qualitative (and semiquantitative) comparisons between these predictions and our data in the range up to $\gamma \approx 10$.

Baldereschi and Lipari (hereafter BL)[15] have developed a perturbation model for an exciton in a zinc-blende or diamond lattice which includes effects due to the degeneracy and anisotropy of the valence band. Essentially they separate the exciton Hamiltonian H_{ex} into two parts, H_s and H_d, where the former is a matrix containing only s-

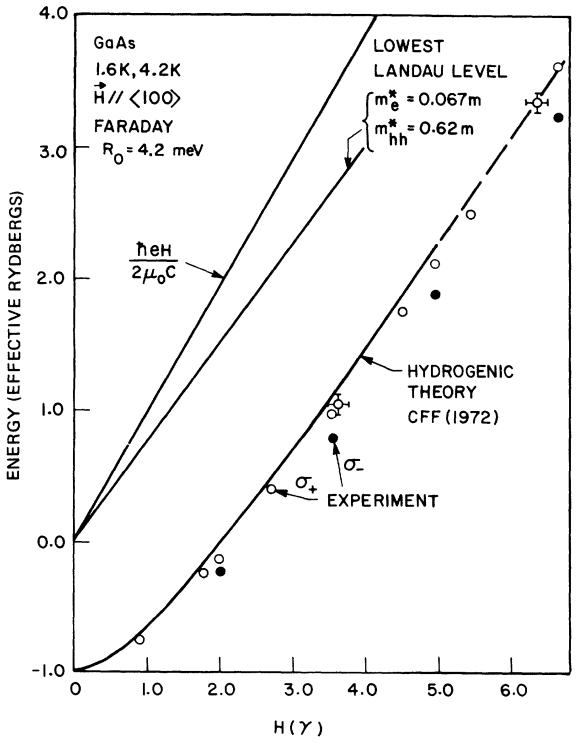

FIG. 2. Comparison between experimental and hydrogenic exciton ground-state energies in a magnetic field. The experimental fields range up to ~220 kG ($\gamma = 1$ when $H = 32$ kG for $R_0 = 4.2$ meV). The agreement between experiment and theory is seen to be good, especially at high fields.

like operators and the latter contains only d-like operators. An additional term, H_P, is required for zinc-blende lattices; however, BL demonstrate that this term may be neglected. The solution for the H_s Hamiltonian is the familiar hydrogen atom result with a reduced mass $\mu_0(1/\mu_0 = 1/m_e^* + \gamma_1/m_0)$ and a dielectric constant ϵ. This leads to an effective rydberg, $R_0 = \mu_0 e^4/2\hbar^2\epsilon^2$, which defines the unit of energy for a specific material. Inclusion of H_d results in a small increase in this hydrogenic binding energy of the exciton ground state. This correction to R_0, which depends upon the valence-band parameters γ_1, γ_2, and γ_3[26] amounts to ~6.5% for GaAs, showing that the perturbation approach should be valid in this material.

Altarelli and Lipari[16] have now extended this perturbation approach to include linear and quadratic magnetic field terms in the low magnetic field limit. The Hamiltonian that they use is $H_{ex} = H_s + H_d + H_l + H_q$, where $H_d + H_l + H_q$ are considered as small perturbations on H_s (H_l represents the linear magnetic field contribution and H_q is the quadratic field term). The final result of this calculation is a set of eight eigenvalues (see Appendix) containing valence-band parameters[26] (γ_1, γ_2, γ_3, κ, q) and conduction-band quantities (m_e^* and g_e) as adjustable parameters.

Using the parameters given by Lawaetz[20] a 6.5% increase in binding energy over the hydrogenic R_0 value is predicted at zero field. The first-order term in γ, the magnetic field, describes the Zeeman splitting of the eightfold-degenerate ground state by this magnetic field. The pattern is symmetrical and obeys a center-of-gravity splitting rule. By taking average values of split components in appropriate polarizations this linear term may be ignored in the consideration of second- or higher-order effects. The second-order term in γ gives rise to a pronounced shift of the lines to higher energies as the field is applied. A consideration of the eigenvalues shows that this shift is different for light propagating with the electric vector parallel to the magnetic field (Voigt geometry, $\vec{E} \parallel \vec{H}$, π) than it is for the electric vector perpendicular to the field (Voigt, $\vec{E} \perp \vec{H}$, σ). For GaAs[16] the shifts are

$$\vec{E} \parallel \vec{H}\ (\pi): \Delta_{\parallel} = [\tfrac{1}{2} - \tfrac{2}{5}\Phi N - \tfrac{1}{2}(\mu_0/\mu_1)]\gamma^2 = 0.382\gamma^2,$$

$$\vec{E} \perp \vec{H}\ (\sigma_{\pm}): \Delta_{\perp} = [\tfrac{1}{2} - \tfrac{2}{5}\Phi N + \tfrac{1}{4}(\mu_0/\mu_1)]\gamma^2 = 0.462\gamma^2,$$

where $\Delta = \frac{1}{2}\gamma^2$ is the hydrogenic value from second-order perturbation theory. The second and third terms (see Appendix) represent corrections arising out of the valence-band complexities.

The "exact" calculation of the hydrogenic shifts given by CFF[12] is generally smaller than $\frac{1}{2}\gamma^2$. In the comparison with experiment we use the CFF value for the hydrogenic term and the corrections to it as given by AL. As we shall see, this leads to better agreement between experiment and theory than that obtained with the AL model alone. For the perturbation approach to be meaningful, the deviation of the shifts from the hydrogenic value should be small. AL suggest that the model applies for $\gamma < 0.4$.

IV. COMPARISON BETWEEN EXPERIMENT AND THEORY

The principal experimental results of this investigation are given in Figs. 2 and 3.

Hydrogenic Approximation: $\gamma < 10$

In Fig. 2 the result for $\vec{H} \parallel \langle 100 \rangle$, Faraday geometry ($\vec{E} \perp \vec{H}$, $\vec{k} \parallel \vec{H}$) is compared with the CFF model with $\gamma \leq 5$. The experimental data go to $\gamma \approx 8$ and, as is evident from the figure, a smooth extrapolation of the theoretical curve to $\gamma > 5$ would continue to give good agreement with experiment. In this figure we have set R_0, the effective Rydberg, equal to the experimentally determined[5,6] exciton binding energy of 4.2 ± 0.2 meV. This is appropriate because in the hydrogenic model these two quantities must be equal at zero magnetic field. The line marked "Lowest Landau Level" is calculated using the mass parameters shown. In the absence of Coulomb effects this is the energy at which the first band-to-band feature is expected to appear. The range of experimental observation

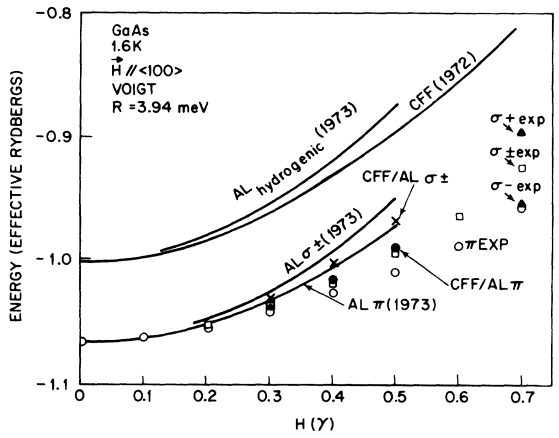

FIG. 3. Comparison between experiment and various theoretical predictions for shifts and average splittings of the free exciton of GaAs in the low magnetic field limit. The curve marked CFF (1972) is from the uncorrected hydrogenic model (Ref. 12). The curves marked AL hydrogenic (1973), AL$\sigma_{\pm}$ (1973), and ALπ (1973) are taken from the Altarelli and Lipari (Ref. 16) second-order perturbation calculation. The points × and ● result when the AL corrections are applied to the CFF hydrogenic results. The experimental results are shown as □ for $\sigma_{\pm}$ and ○ for π and they are always equal to or below the theoretical predictions.

extended above the position of this line at all field strengths. In no instance was any structure found above that which is attributed to the lowest exciton state. These observations agree well with the predictions of Elliott and Loudon.[8]

In the range of γ where we have reliable photoelectrically recorded reflectance intensity data, $\gamma < 3$, we find good semiquantitative agreement with the intensity calculation of CFF. Above $\gamma = 3$, where photographic techniques were used, the reflectance intensity increased markedly over the $\gamma = 0$ value as the field was increased to $\gamma > 8$. Again, this is as predicted by Elliott and Loudon.[8]

In summary, the hydrogenic model gives a very reasonable description of the free exciton in GaAs in magnetic fields up to about $\gamma \approx 10$. This applies specifically to the energy and to the intensity of the $1s$ exciton creation transition.

Zinc-Blende Approximation: Low-Field Limit–Quadratic Contributions

Turning to the low-field limit, $\gamma \leq 0.5$, we compare the experimental results (Voigt, $\vec{H} \parallel \langle 100 \rangle$, $\vec{E} \parallel \vec{H}: \pi$, $\vec{E} \perp \vec{H}: \sigma_{\pm}$)[27] with the hydrogenic model as well as with that due to AL and that due to CFF, but with the AL corrections applied (Fig. 3). At $\gamma = 0$ the hydrogenic model gives a binding energy of R_0. The AL model binding energy is $1.065R_0$ and this latter value is set equal to the experimental exciton binding energy of 4.2 meV, leading to $R_0 = 3.94$ meV ($\mu_0/m_0 = 0.045$).

Initially, the AL model predicts the correct sense of polarization splitting, $E_{\sigma_\pm} > E_\pi$ and $E_{\sigma_-} < E_{\sigma_+}$, although the shift of these energies with field is overestimated by 50% at $\gamma = 0.4$. Using the CFF hydrogenic model corrected by the AL valence-band terms improves the situation, bringing experiment and theory to within about 20% at $\gamma = 0.4$. The inclusion of higher-order terms in the AL corrections would improve the correspondence between theory and experiment and may well bring the theory within the error range of the experiment.[28] At this point the CFF hydrogenic theory, corrected by the AL valence-band anisotropy and degeneracy terms, gives a satisfactory description of the GaAs exciton energies in the low-field limit.

Low-Field Limit: Linear Zeeman Contributions

The eight components of the exciton ground state give rise to six allowed exciton creation transitions when the magnetic field is directed along a $\langle 100 \rangle$ axis of the sample. It is straightforward to show that in the group of the magnetic field (S_4 when $\vec{H} \parallel \langle 100 \rangle$) there will be four allowed σ transitions (two in σ_+ and two in σ_- with intensity ratios of 3:1 in each polarization) and two allowed π transitions (of equal intensity). The actual splittings between these transitions can be given (Appendix) in terms of valence-band and conduction-band parameters κ, q, g_e, μ_0/m_0, and $(\mu_0/\mu_2)^2$ with appropriate scale factors. There is good support[20] for the notion that $\kappa \gg q$ and that g_e and $(\mu_0/\mu_2)^2$ are small in GaAs. Using the parameters given in the compilation of Lawaetz[20] one predicts a splitting of $0.56R_0$ between σ_+ and σ_- at $\gamma = 1$, whereas the experimentally determined splitting is $\sim 0.1R_0$ ($g_{\text{eff}} = 1.70$). As the terms in q, g_e, and $(\mu_0/\mu_2)^2$ make small contributions compared to that of κ it appears that $\kappa(\text{GaAs})^{20} = 1.72$ is too large. A recent evaluation[21,22] of a number of experiments in GaAs produces a range of 0.8–1.5 for κ. Even the lowest value of $\kappa = 0.8$ is still too large to explain our Zeeman splitting data.

Another check on these parameters is provided by the fact that the theory predicts two π components of equal intensity with a separation of $(0.09\kappa - 0.08)$ at $\gamma = 1$ if $q = g_e = 0$. There is no suggestion of two components in our π spectra at $\gamma = 2$, even though our resolution is better than $0.05R_0$ in this

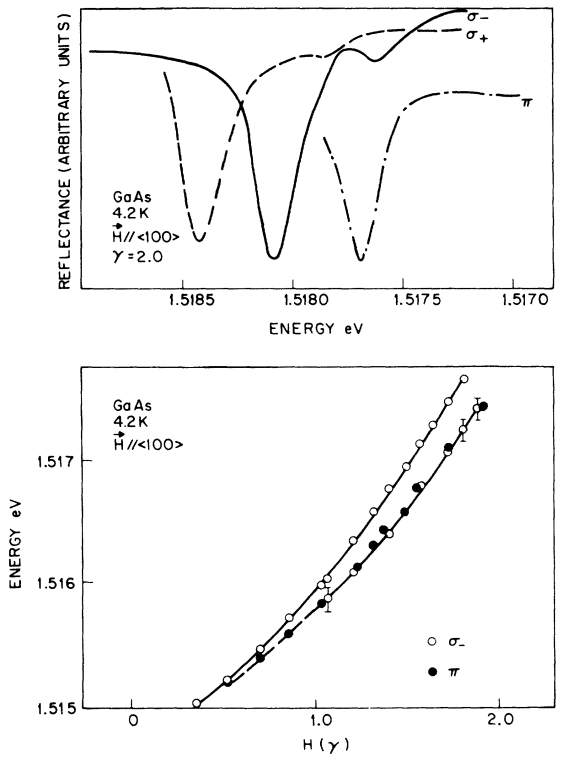

FIG. 4. (a) Typical experimental traces at $\gamma = 2$ in the σ_+ (Faraday, right circularly polarized light), the σ_-, and the π (Voigt, $\vec{E} \parallel \vec{H}$) configurations. The weak structure in σ_+ (an equivalent feature, but more clearly resolved is seen, in σ_-) is very close to the energy of the main π feature (see text). (b) The energy of the various σ_+, σ_-, and π features is shown as a function of magnetic field in the range $1 \lesssim \gamma \lesssim 2$. The convergence of all features with decreasing field is evident.

polarization (Fig. 4), and hence $0.5 < \kappa < 1.2$ appears to be an appropriate range for κ.

One further check on the qualitative features of the splitting pattern is given by the fact that when $g_e \approx 0$, the weaker of the σ_- and σ_+ components should lie at energies lower than their stronger partner. Furthermore, they should be close to the energy of the (unresolved?) π lines since they are subject to the same quadratic shift as are the π lines. At $\gamma = 2$ (Fig. 4) weak structure is seen on the low-energy side of both the prominent σ_+ and σ_- features. These weak features are close to the energy of the π feature and we expect that they are indeed due to the weaker σ_+ and σ_- components. By following the splitting of the σ_+ or the σ_- lines as a function of field it may be shown that they originate from the zero-field free-exciton structure (Fig. 4) and thus the possibility that the weak features are impurity related is eliminated.

Due to difficulties associated with background and line shapes it is not possible to give accurate energies for these weak features in the low-field limit and hence a quantitative comparison with the theory is not possible. The qualitative features, however, are quite consistent with the AL model and it remains to ascertain values of κ, q, and $\bar{\mu}^*$ from other, independent studies. The extension of this study to other zinc-blende semiconductors, which have well-characterized valence bands, is underway, and these results may shed light upon the above-mentioned difficulties with the first-order splittings in GaAs.

Low-temperature high-resolution reflectivity data have been taken in the band-edge region of GaAs layers in the presence of externally applied magnetic fields. A comparison of these results with the predictions of the simple hydrogenic exciton model as well as with a more detailed model, which includes the valence-band complications of a zinc-blende structure, demonstrates the excitonic nature of the spectrum as well as giving good support to the general utility of both theories in the description of excitons in small and large magnetic fields.

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APPENDIX

The eight eigenvalues that correspond to the ground state of a direct exciton in a zinc-blende structure in the presence of a magnetic field, as given by Altarelli and Lipari,[16] are

$$E_1 = -1 - \tfrac{4}{5}\Phi S_1 + [(3\kappa + \tfrac{27}{4}q \pm \tfrac{1}{2}\bar{\mu}^*)(\mu_0/m_0) + \tfrac{8}{15}(\mu_0/\mu_2)^2 M]\gamma + [\tfrac{1}{2} - \tfrac{2}{5}\Phi N + \tfrac{1}{2}(\mu_0/\mu_1)]\gamma^2,$$

$$E_2 = -1 - \tfrac{4}{5}\Phi S_1 + [(\kappa + \tfrac{1}{4}q \pm \tfrac{1}{2}\bar{\mu}^*)(\mu_0/m_0) - \tfrac{8}{15}(\mu_0/\mu_2)^2 M]\gamma + [\tfrac{1}{2} - \tfrac{2}{5}\Phi N - \tfrac{1}{2}(\mu_0/\mu_1)]\gamma^2,$$

$$E_3 = -1 - \tfrac{4}{5}\Phi S_1 + [(-\kappa - \tfrac{1}{4}q \pm \tfrac{1}{2}\bar{\mu}^*)(\mu_0/m_0) + \tfrac{8}{15}(\mu_0/\mu_2)^2 M]\gamma + [\tfrac{1}{2} - \tfrac{2}{5}\Phi N - \tfrac{1}{2}(\mu_0/\mu_1)]\gamma^2,$$

$$E_4 = -1 - \tfrac{4}{5}\Phi S_1 + [(-3\kappa - \tfrac{27}{4}q \pm \tfrac{1}{2}\bar{\mu}^*)(\mu_0/m_0) - \tfrac{8}{15}(\mu_0/\mu_2)^2 M]\gamma + [\tfrac{1}{2} - \tfrac{2}{5}\Phi N + \tfrac{1}{2}(\mu_0/\mu_1)]\gamma^2,$$

where N, S_1, and M are numerical constants, $N = 0.4687$, $S_1 = 0.2246$, and $M = 0.2812$,

$$\Phi = 8(\mu_0/\mu_1)^2 + (\mu_0/\mu_2)^2 ;$$

$\bar{\mu}^*$ is the electron effective magnetic moment in effective Bohr magnetons and μ_0, μ_1, and μ_2 are related to the usual Luttinger[26] mass parameters through the equalities

$$1/\mu_0 = 1/m_e^* + \gamma_1/m_0,$$

$$1/\mu_1 = \gamma_2/m_0,$$

$$1/\mu_2 = 2\sqrt{3}\,(\gamma_3/m_0),$$

m_0 is the free-electron mass. κ and q are as defined by Luttinger[26] and $\gamma = eH/2\mu_0 cR_0$.

*Permanent address: Bell Laboratories, Murray Hill, N. J. 07974.

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[28]At $\gamma = 0.4$ the shift in the π line is $0.04R_0$ ($\approx 0.05R_0$ for $\sigma_\pm$) which amounts to about 0.16 meV. This energy is similar to the expected splitting, at zero field, of Γ_5 and $\Gamma_4 + \Gamma_3$ due to electron-hole exchange (Refs. 18 and 19) and hence the neglect of this latter splitting is probably not warranted in the low-field range. For this reason alone, we do not expect to reach perfect agreement between experiment and the AL calculation which neglects all exchange interactions. Our inability to resolve a second π line in this low-field regime may also be related to this point; namely, the "second" π line comes from the zero-field forbidden Γ_4 ($J = 2$) exciton state and at low fields this may still be too weak to observe in our experiments. In the AL model the two π lines are expected to be equally intense under all low-field conditions.