Fine structure of excitons in type-II GaAs/AlAs quantum wells

H. W. van Kesteren, E. C. Cosman, and W. A. J. A. van der Poel
Philips Research Laboratories, NL-5600 JA Eindhoven, The Netherlands

C. T. Foxon
Philips Research Laboratories, Redhill, Surrey RH1 5HA, England
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Optically detected magnetic resonance in zero field as well as in a finite magnetic field has been used to study the excitons in type-II GaAs/AlAs quantum wells. The spectra are analyzed using the appropriate spin Hamiltonian for the quasi-two-dimensional indirect excitons. The electron-hole exchange interaction and the g factors for the electron and hole are obtained for several thicknesses of the GaAs and AlAs layers. Good agreement exists between the trend in the exchange interaction and the effective-mass theory of Rejaei Salmassi and Bauer. The anisotropy of the electron g factor is in accordance with a lifting of the threefold degeneracy of the AlAs X conduction-band minimum by the quantum-well potential giving the X_z valley the lowest energy in the thin-layer quantum wells studied. The effective heavy-hole g value of ~ 2.5 is much smaller than in the bulk and depends on the GaAs well thickness. This is probably a consequence of the valence-band mixing in quantum-well structures. Two classes of excitons are observed, each with a symmetry that is lower than the anticipated D_{2d} point-group symmetry for excitons in quantum wells. The actual symmetry of the type-II excitons and the width of the exciton resonances are related to the microscopic structure of the GaAs/AlAs interface.

I. INTRODUCTION

Excitons play an important role in the optical properties of semiconductors, especially for undoped quantum wells and superlattices for which the optical transitions are usually intrinsic in origin. The optical transitions associated with these excitons in heterostructures, both with and without external perturbations, have been extensively studied. However, the fine structure of the quasi-two-dimensional excitons has not received much interest up to now. For instance, the magnitude of the electron-hole exchange interaction and the magnitude of the spin splittings of the exciton in a magnetic field are not yet well known. The exchange coupling is expected to be enhanced in quantum wells due to the confinement of the carriers. In type-I GaAs/AlAs quantum wells, a splitting of the photoluminescence line of a few meV which varied with the well thickness has been interpreted as being due to the exchange interaction.[1,2] The electron and hole spin splittings in a magnetic field and their dependence on the well thickness and on the orientation of the quantum well with respect to the magnetic field direction are of interest because they are related to the microscopic structure of the excitons and to the band structure of the quantum well.

Optically detected magnetic resonance (ODMR) is a powerful technique to unravel the fine structure of the excitons.[3] However, a limitation of this technique is that the recombination rate of the excitons should be comparable to or less than the microwave-induced transition rate between the exchange and magnetic-field-split exciton levels, i.e., the lifetime has to be at least a few tenths of a microsecond. Recently, we showed that the excitons in type-II GaAs/AlAs quantum wells can be studied by ODMR.[4] In these type-II structures, the electron and hole forming the exciton are confined in spatially separate wells. Due to the spatial as well as **k**-space indirectness, the exciton lifetime in these structures is in the microsecond range.[5]

From photoluminescence studies on these systems it is known that a type-II band alignment in the GaAs/AlAs system is obtained when the GaAs thickness is less than ~ 35 Å.[6,7] This is due to the fractional Γ conduction-band offset of ~ 0.67 and to the fact that AlAs is an indirect and GaAs a direct semiconductor with the lowest conduction band at the X and Γ point, respectively. When the confinement energy for the electrons in the GaAs layer exceeds the sum of the GaAs Γ to AlAs X conduction-band offset and the AlAs X confinement energy, a type-II alignment is obtained with the electrons confined in the AlAs layer and the holes in the GaAs layer.

In a previous publication[8] we reported on the results obtained from the anisotropy of the optically detected resonance of the electrons. The angular dependence of the electron spin g value in a series of type-II samples revealed the influence of confinement and lattice mismatch strain on the lifting of the threefold degeneracy of the AlAs X conduction-band minima. The purpose of this paper is to describe the results of an ODMR investigation of the excitons in a series of type-II GaAs/AlAs multiple quantum wells with varying GaAs and AlAs thicknesses. ODMR spectra have been recorded in zero-field as well as in a finite magnetic field. The zero- and magnetic-field spectra together with the anisotropy of the resonances as a function of the orientation of the magnetic field with respect to the quantum-well axes are analyzed using the spin-Hamiltonian formalism. The ODMR spectra of the excitons provide a high-precision measurement of the exchange interaction as a function of the electron-hole separation, which is determined by the GaAs and AlAs thicknesses. Because the exchange interaction is in the μeV range, these exchange splittings cannot be resolved in the optical spectra. Furthermore, it will be shown that the actual symmetry of the excitons and the width of the exciton resonances provide information about the microscopic structure of the GaAs/AlAs interface.

II. EXPERIMENTAL

The samples used in this study were grown by molecular-beam epitaxy (MBE). The layers were deposited on (001)-oriented semi-insulating or n-type GaAs substrates at a temperature of 630–650 °C. They consisted of 1.0 μm of GaAs buffer material, 60–348 periods of GaAs/AlAs where the number depends on the thickness of the layers, and finally a capping layer of 0.1 μm of GaAs. The GaAs and AlAs thicknesses for the various samples are given in Table I.

The ODMR experiments were carried out with the sample immersed in liquid helium having a temperature of 1.6 K. For the photoexcitation laser light was used with an energy greater than the band gap of GaAs. The excitation power density on the sample was about 1 W/cm^2. The type-II luminescence was filtered out and detected with a photomultiplier. The ODMR spectra were recorded either without a magnetic field by varying the microwave frequency, or in a magnetic field using a fixed microwave frequency and a varying magnetic field strength. For the zero-field ODMR measurements the sample was mounted within a one-turn coil. The power from the microwave source was in a 1–100-mW range. ODMR spectra were recorded with phase-sensitive detection of the difference between the polarized components of the luminescence using a photoelastic modulator operating at 50 kHz. The microwave frequency was scanned slowly and the spectra were averaged up to 32 times. The ODMR experiments in a magnetic field were carried out at a fixed frequency of ~10 GHz and a microwave power incident on the cavity of about 100 mW. For the phase-sensitive detection either the amplitude of the microwaves was chopped using a pin modulator or the polarization direction of the detected luminescence using a photoelastic modulator.

III. ODMR SPECTRA

The analysis of the ODMR spectra of the type-II GaAs/AlAs quantum wells is carried out using the spin-Hamiltonian formalism. The appropriate Hamiltonians are obtained from symmetry considerations only and the experimental results are thereafter expressed in terms of several parameters adjusted to fit the spectra. These parameters can be compared with, for instance, effective-mass theory results.

A. Spin Hamiltonian

In order to enable a comparison between the results for three-dimensional and quasi-two-dimensional excitons, we will first consider the Hamiltonian for bulk excitons. The exciton ground state in a bulk indirect $Al_xGa_{1-x}As$ semiconductor is made of an electron with spin $S_e=\frac{1}{2}$ associated with the X conduction-band minimum and a hole with $J_h=\frac{3}{2}$ associated with the Γ valence-band maximum. To deduce the Hamiltonian, we make use of the fact that the total Hamiltonian must retain its scalar form under the coordinate transformations of the T_d group.[9,10] Because $(S_{e,x},S_{e,y},S_{e,z})$ and $(J_{h,x},J_{h,y},J_{h,z})$, $(J^3_{h,x},J^3_{h,y},J^3_{h,z})$ as well as the magnetic field components (B_x,B_y,B_z) belong to the Γ_4 representation, the exciton Hamiltonian

$$H_{ex}=H_e+H_h+H_{e\text{-}h} \tag{1}$$

can be written as

$$H_e=\mu_B g_e \sum_{i=x,y,z} S_{e,i}B_i \tag{1a}$$

and

$$H_h=-2\mu_B \sum_{i=x,y,z} (\kappa J_{h,i}+qJ^3_{h,i})B_i \tag{1b}$$

TABLE I. Sample identifier, nominal GaAs and AlAs thickness (the number between parentheses is the thickness as obtained from x-ray diffraction combined with photoluminescence excitation spectroscopy), and exchange splitting parameters.

			$B=0$ T			B‖[001]	B‖[110]/[1$\bar{1}$0]	
			c_x	c_y	c_z	c_z	c_x	c_y
Sample	GaAs (Å)	AlAs (Å)		(μeV) (±25%)		(μeV) (±5%)	(μeV) (±25%)	
No. 1 (G345)	14	14				34.0		
No. 2 (G340)	17	17				17.0	2.5	4.5
No. 3 (G485)	17	17				19.1	4.5	5.5
No. 4 (G264)	25(22)	17(19)	$c_x+c_y=3$			8.5	1.4	2.2
No. 5 (G261)	25(23)	25(28)	0.4	1.1	3.3	3.4	0.7	1.0
No. 6 (G262)	25(23)	42(41)	0.3	0.4	1.3	1.4	<0.5	<0.5

describing the Zeeman splittings of the electrons and holes respectively, and

$$H_{e\text{-}h}=-\sum_{i=x,y,z}(aJ_{h,i}S_{e,i}+bJ_{h,i}^{3}S_{e,i}) \quad (1c)$$

describing the spin-spin coupling of the electron and hole forming the exciton. The spin-spin coupling can include exchange, magnetic dipole-dipole, and higher multipole interactions. In these expressions μ_B is the Bohr magneton, g_e,κ,q are the (Luttinger) Zeeman splitting constants for the electron and hole, and a,b the spin-spin coupling constants. The cubic terms in the hole-Zeeman and in the spin-spin interaction Hamiltonian are mostly much smaller than the linear terms and can usually be neglected.

For a (001)-grown quantum well, the relevant symmetry is D_{2d}. The upper valence band is split into a light-hole band with $J_{h,z}=\pm\frac{1}{2}$ and a heavy-hole band with $J_{h,z}=\pm\frac{3}{2}$. For the magnetic fields used in the ODMR experiments the light and heavy-hole energy splittings are much smaller than the difference in the subband energy for the light and heavy holes. This means that we can describe the magnetic properties of the light- and heavy holes separately, using only the 2×2 submatrices for the $J_{h,z}=\pm\frac{1}{2}$ and $J_{h,z}=\pm\frac{3}{2}$ states, respectively. At low temperatures the hole occupies the $J_{h,z}=\pm\frac{3}{2}$ states and we are left with the heavy-hole 2×2 submatrices only. These heavy-hole submatrices have the property that $\tilde{J}_{h,x}=\tilde{J}_{h,y}=0$ and $\tilde{J}_{h,z}=\frac{4}{9}\tilde{J}_{h,z}^{3}$. For the D_{2d} symmetry, $(S_{e,x},S_{e,y})$, $(\tilde{J}_{h,x}^{3},\tilde{J}_{h,y}^{3})$, and (B_x,B_y) belong to the Γ_5 while $S_{e,z},\tilde{J}_{h,z}^{3}$ and B_z belong to the Γ_2 representation. Therefore, H_{ex} is given by

$$\begin{aligned}H_{\text{ex}}=&\sum_{i=x,y}[\mu_B(g_{e,i}S_{e,i}-2q_i\tilde{J}_{h,i}^{3})B_i-b_iS_{e,i}\tilde{J}_{h,i}^{3}]\\&+\mu_B[g_{e,z}S_{e,z}-(\tfrac{8}{9}\kappa_z+2q_z)\tilde{J}_{h,z}^{3}]B_z\\&-(\tfrac{4}{9}a_z+b_z)S_{e,z}\tilde{J}_{h,z}^{3}\end{aligned} \quad (2)$$

with $g_{e,x}=g_{e,y}$, $q_x=q_y$, and $b_x=b_y$. By using an effective heavy-hole spin $\tilde{S}_h=\frac{1}{2}$, this expression can be written in the form

$$H_{\text{ex}}=\sum_{i=x,y,z}[\mu_B(g_{e,i}S_{e,i}-g_{h,i}\tilde{S}_{h,i})B_i-c_iS_{e,i}\tilde{S}_{h,i}]\ . \quad (3)$$

When we identify the $J_{h,z}=+\frac{3}{2}$ with the $\tilde{S}_{h,z}=+\frac{1}{2}$ state and $J_{h,z}=-\frac{3}{2}$ with $\tilde{S}_{h,z}=-\frac{1}{2}$, the coefficients in the spin Hamiltonians (2) and (3) are related by

$$g_{h,x}=3q_x,\quad g_{h,y}=-3q_y,\quad g_{h,z}=6\kappa_z+13.5q_z\ ,$$

$$c_x=1.5b_x,\quad c_y=-1.5b_y,\quad c_z=3a_z+6.75b_z\ ,$$

for the D_{2d} point-group symmetry $g_{h,x}=-g_{h,y}$ and $c_x=-c_y$. Anticipating the experimental results, we also consider the Hamiltonian for the lower-symmetry point groups C_{2v}, D_2, C_2, and C_s. For these symmetries, $S_{e,x}$, $S_{e,y}$, $S_{e,z}$, and similarly $\tilde{J}_{h,i}^{3}$ and B_i all belong to different representations. This implies that all the coefficients in expression (2) have a different magnitude and the axial symmetry along the z axis no longer exists.

B. Results

To study the spin-spin interaction without the complication of extra splittings due to an external magnetic field, ODMR spectra have been recorded without any magnetic field. Zero-field spectra for two samples with (25 Å GaAs)/(42 Å AlAs) and (25 Å GaAs)/(25 Å AlAs) are shown in Figs. 1(a) and 1(b). Resonance lines could only be observed by detecting changes in the degree of linear polarization along the [110] and [1$\bar{1}$0] axes of the quantum well and not in the circular components of the luminescence. Furthermore, the spectra differed depend-

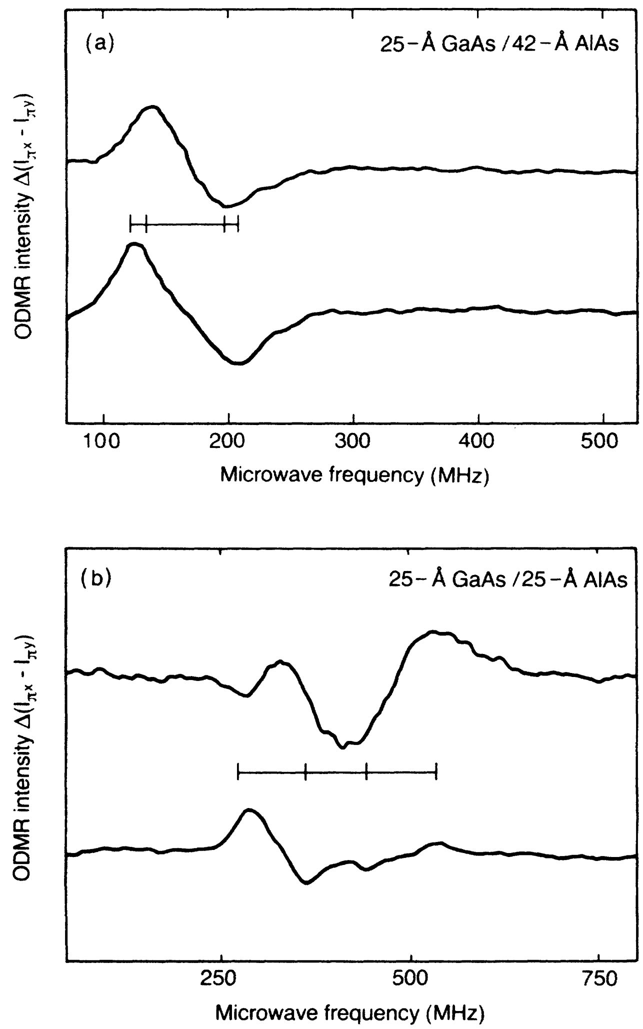

FIG. 1. Zero-field ODMR spectra for (a) the (25 Å GaAs)/(42 Å AlAs) and (b) the (25 Å GaAs)/(25 Å AlAs) sample. The signals correspond to changes in the degree of linear polarization along the principal [110] and [1$\bar{1}$0] axes. The two spectra in each figure have been obtained for perpendicular directions of the microwave field, i.e., along each of the principal axes. The line positions used to obtain the exchange splitting parameters are indicated also.

ing on whether the direction of the microwave magnetic field was along the [110] or along the [1$\bar{1}$0] axis. For the (25 Å GaAs)/(42 Å AlAs) sample, the ODMR spectrum consists of two overlapping lines with opposite polarity. The spectrum for the (25 Å GaAs)/(25 Å AlAs) is better resolved and shows four lines.

To explain this, we consider the zero-field exciton energy levels in the D_{2d} quantum-well symmetry and in the lower symmetries. The radiative properties of the zero-field states can be understood best in the $J_{h,z} = \pm\frac{3}{2}$ picture of the heavy hole. The foregoing theoretical treatment revealed that for D_{2d} symmetry $c_x = -c_y$. As a result, the dipole allowed radiative levels $|J_{h,z} = \pm\frac{3}{2}, S_{e,z} = \mp\frac{1}{2}\rangle$ are degenerate and there are only splittings between the radiative and nonradiative states and between the two nonradiative states. For microwaves with a magnetic field component in the plane of the quantum well, two transitions can be induced with transition probabilities that do not depend on the actual direction of the microwave magnetic field with respect to the quantum-well axes. For the lower symmetry cases, $|c_x|$ and $|c_y|$ are different in magnitude and the radiative doublet is also split. In Fig. 2 the zero-field levels together with their radiative properties and the allowed microwave transitions are shown for D_{2d} and for a lower symmetry. The split optically active states decay by the emission of light, linearly polarized along the principal in-plane axes. In the lower symmetry, four transitions can be observed for microwaves with a magnetic field component in the plane of the quantum well. These transitions have their maximum intensity when the microwave magnetic field is along one of the principal directions.

The experimental finding of four resonance lines for the (25 Å GaAs)/(25 Å AlAs) sample is only compatible with a symmetry lower than D_{2d}. The difference of the ODMR spectra for the two orientations of the microwave field further supports the idea of a symmetry lowering. For the (25 Å GaAs)/(42 Å AlAs) sample the extrema of the resonance lines occur at slightly different microwave frequencies for the two directions of the microwave field. This also shows that for this sample the symmetry is lower than D_{2d}. The direction of the linear polarization components along [110] and [1$\bar{1}$0] as well as the dependence on the microwave field along these two directions indicate that the principal in-plane axes are along [110] and [1$\bar{1}$0]. The magnitudes of c_x, c_y, and c_z obtained from the zero-field spectra are given in Table I.

ODMR spectra in a magnetic field have been obtained with the field along each of the principal [110], [1$\bar{1}$0], and [001] axes. In Fig. 3, ODMR spectra with the field perpendicular to the quantum-well plane are shown for three samples with a fixed GaAs thickness of 25 Å and a varying AlAs thickness. The spectra were recorded by monitoring changes in the degree of circular polarization. For these measurements, the luminescence is detected along the direction of the magnetic field. Three lines are generally observed in the spectra. These lines have previously been identified as belonging to two systems: the outer two lines correspond to electron spin transitions of the heavy-hole exciton split apart by the spin-spin interaction, while the line in between is ascribed to the unbound electrons in the AlAs layer.[4] The different origin of the ODMR lines can be inferred from the different dependence of the resonance line intensities on the excitation power density. For low excitation only the exciton resonances are observed, while for increasing power densities the electron spin resonance increases faster than the exciton resonances.

The four exciton states for a magnetic field perpendicular to the quantum-well plane are in good approximation given by $|\pm\frac{3}{2}, \mp\frac{1}{2}\rangle$ for the states decaying by the emission of circularly polarized light and $|\pm\frac{3}{2}, \pm\frac{1}{2}\rangle$ for the

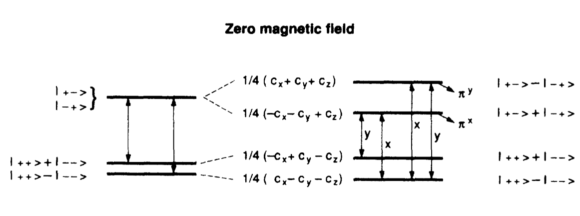

FIG. 2. Zero-field energy levels, radiative properties, and allowed microwave transitions for excitons in D_{2d} and in a lower symmetry. Where the microwave transition rate depends on the direction of the microwave magnetic field, the direction for the maximum rate is also shown.

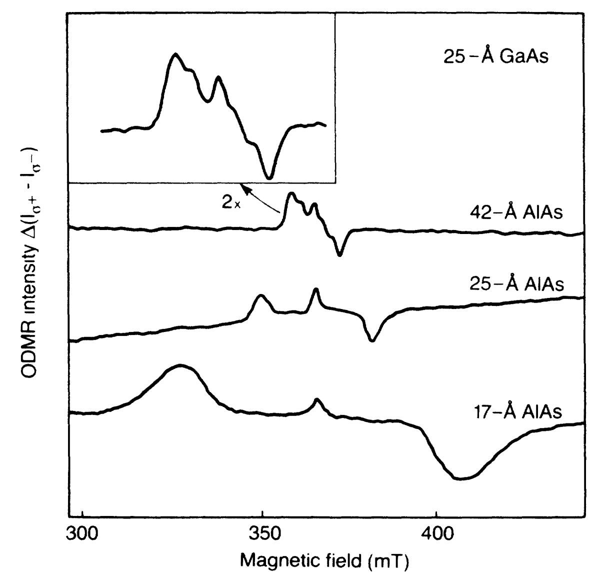

FIG. 3. ODMR spectra with the magnetic field perpendicular to the quantum-well plane for three samples with a GaAs well thickness of 25 Å and a varying AlAs thickness. The signals correspond to changes in the degree of circular polarization. The inset shows the resonances for the 42 Å sample enlarged by a factor of 2 to clarify the extra structure on the exciton resonance lines.

nonradiative states. The two allowed microwave transitions for the exciton correspond to electron spin flips and connect a nonemitting level with an emitting one (Fig. 4). The resonance condition for these transitions is given by

$$h\nu = G_+ + G_- \pm \tfrac{1}{2}c_z \tag{4}$$

with

$$G_\pm = [\tfrac{1}{4}\mu_B^2 B_z^2 (g_{e,z} \pm g_{h,z})^2 + \tfrac{1}{16}(c_x \pm c_y)^2]^{1/2} . \tag{4a}$$

The c_z parameter is obtained directly from the splitting of the exciton resonances (Table I). For those samples that were also studied in zero field, the c_z values are in good agreement with the ones obtained from the spectra in a magnetic field. Especially for the samples with the larger splittings the exciton resonances occur asymmetrically with respect to the electron spin resonance. For instance, the splitting between the low field and high field exciton resonance, respectively, and the electron spin resonance amounts to 38.0 and 40.5 mT for the (25 Å GaAs)/(25 Å AlAs) sample while these splittings are 82.0 and 91.0 mT for the (17 Å GaAs)/(17 Å AlAs) (G485) sample. From Eq. (4) it is clear that an asymmetry is always expected for a finite spin-spin coupling but a relatively large asymmetry occurs for $g_{e,z} \simeq -g_{h,z}$ when $c_x \neq -c_y$, i.e., when the symmetry is lower than D_{2d}. That $g_{e,z}$ and $g_{h,z}$ have opposite signs [using the sign convention of Hamiltonian (3)] and have similar absolute values will be shown later on. Using the g and c constants given in Tables I and II, the experimentally observed asymmetry is found to be in good agreement with the one obtained with Eq. (4). So the asymmetry in the ODMR spectra with the field perpendicular to the quantum-well plane supports the finding from the zero-field spectra that the exciton symmetry is lower than D_{2d}. The extra structure which is observed on the exciton resonances for the (25 Å GaAs)/(42 Å AlAs) sample will be discussed in the next section.

ODMR spectra with the magnetic field in the plane of the quantum well could only be detected with the field parallel to or within about 20° of a [110] or [1$\bar{1}$0] axis. Only the (25 Å GaAs)/(17 Å AlAs) sample showed a reasonably resolved in-plane spectrum (Fig. 5). The ODMR spectrum, detected as changes in the degree of linear polarization, shows four lines with one main splitting and two smaller but similar splittings. The splitting pattern is the same for the field along the [110] and [1$\bar{1}$0] axes but the relative magnitude of the signals is different

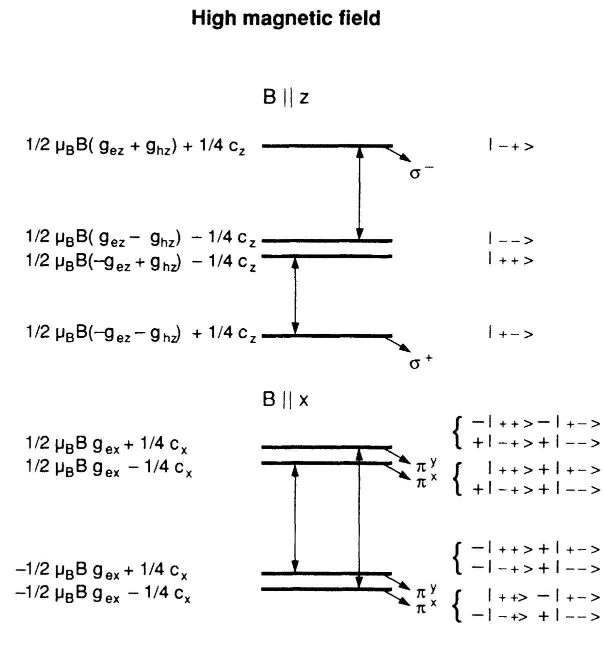

FIG. 4. Energy levels, radiative properties, and allowed microwave transitions for excitons in a relatively high magnetic field where the Zeeman splittings are large compared to the spin-spin splittings. Here, e.g., $|++\rangle$ denotes $|J_{h,z}=+\tfrac{3}{2}, S_{e,z}=+\tfrac{1}{2}\rangle$ or $|\tilde{S}_{h,z}=+\tfrac{1}{2}, S_{e,z}=+\tfrac{1}{2}\rangle$ for the effective $\tilde{S}_h=\tfrac{1}{2}$ description of the heavy hole.

for these two orientations. In the in-plane spectra all resonance lines correspond to one spin system, as could be inferred from the similar laser excitation power dependence of all the lines. The small in-plane splittings can only be due to the $\tilde{S}_{h,x}B_x, \tilde{S}_{h,y}B_y$ hole Zeeman interaction or the $\tilde{S}_{h,x}S_{e,x}, \tilde{S}_{h,y}S_{e,y}$ spin-spin coupling. The fact that the main in-plane splitting for all the samples scales with the magnitude of the spin-spin coupling previously obtained from the ODMR spectra with the field perpendicular to the quantum-well plane, and the fact that the magnitude of the main in-plane splitting for the (25 Å GaAs)/(17 Å AlAs), (25 Å GaAs)/(25 Å AlAs), and (25 Å GaAs)/(42 Å AlAs) samples is in quite good agreement with the splitting calculated from the c_x, c_y spin-spin coupling coefficients obtained from the zero-field spectra, shows that the spin-spin coupling and not the hole-Zeeman interaction is the origin of the in-plane splittings.

TABLE II. Sample identifier, nominal GaAs and AlAs thickness, and electron and hole g values.

Sample	GaAs (Å)	AlAs (Å)	$g_{e,x}=g_{e,y}$ ($\pm$0.005)	$g_{e,z}$ ($\pm$0.003)	$g_{h,x}, g_{h,y}$	$g_{h,z}$ ($\pm$0.1)
No. 1	14	14		1.907		
No. 2	17	17	1.977	1.899	<0.01	
No. 3	17	17	1.977	1.901	<0.01	2.9
No. 4	25	17	1.969	1.892	<0.01	2.3
No. 5	25	25	1.975	1.888	<0.01	2.3
No. 6	25	42	1.975	1.883	<0.01	2.3

However, the pattern of the in-plane ODMR spectra does not agree with a simple spin-spin splitting. This is due to the fact that the spin-spin interaction splits the two highest and lowest energy levels by the same amount, giving four transitions of which two occur at the same field (Fig. 4). Furthermore, two transitions are forbidden and connect levels with the same radiative properties. Therefore we would not expect a four-line spectrum.

From the analysis of the zero-field and perpendicular magnetic-field spectra it is clear that $|c_x|$ and $|c_y|$ have different magnitudes. To explain the four-line spectrum, we assume that there are two classes of excitons with their x and y axes interchanged. In zero field, the ODMR transitions for the two classes of excitons occur at the same microwave frequencies. However, with an in-plane magnetic field the transitions for these two classes occur at different fields. The assumption of two classes of excitons with their respective x and y axes interchanged can therefore explain the observation of four resonance lines. For the magnetic field along one of the principal in-plane axes, the outer resonance lines correspond to one class and the inner two to the other, while for the other principal in-plane orientation the assignment of the classes is reversed. Indeed, comparing the c_x and c_y values obtained in this way with the zero-field values shows that the agreement is quite good. Furthermore, the polarities of the signals for the in-plane spectra reveal that for one class c_x and c_y have the same sign

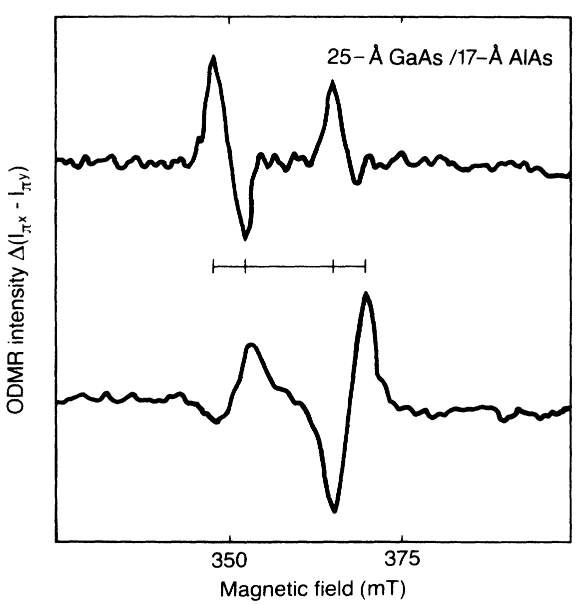

FIG. 5. ODMR spectra for the (25 Å GaAs/(17 Å AlAs) sample with the magnetic field parallel to the [110] and [1$\bar{1}$0] axes, respectively. Resonances correspond to changes in the degree of linear polarization of the luminescence. The line positions used to obtain the in-plane parameters given in Tables I and II are indicated also.

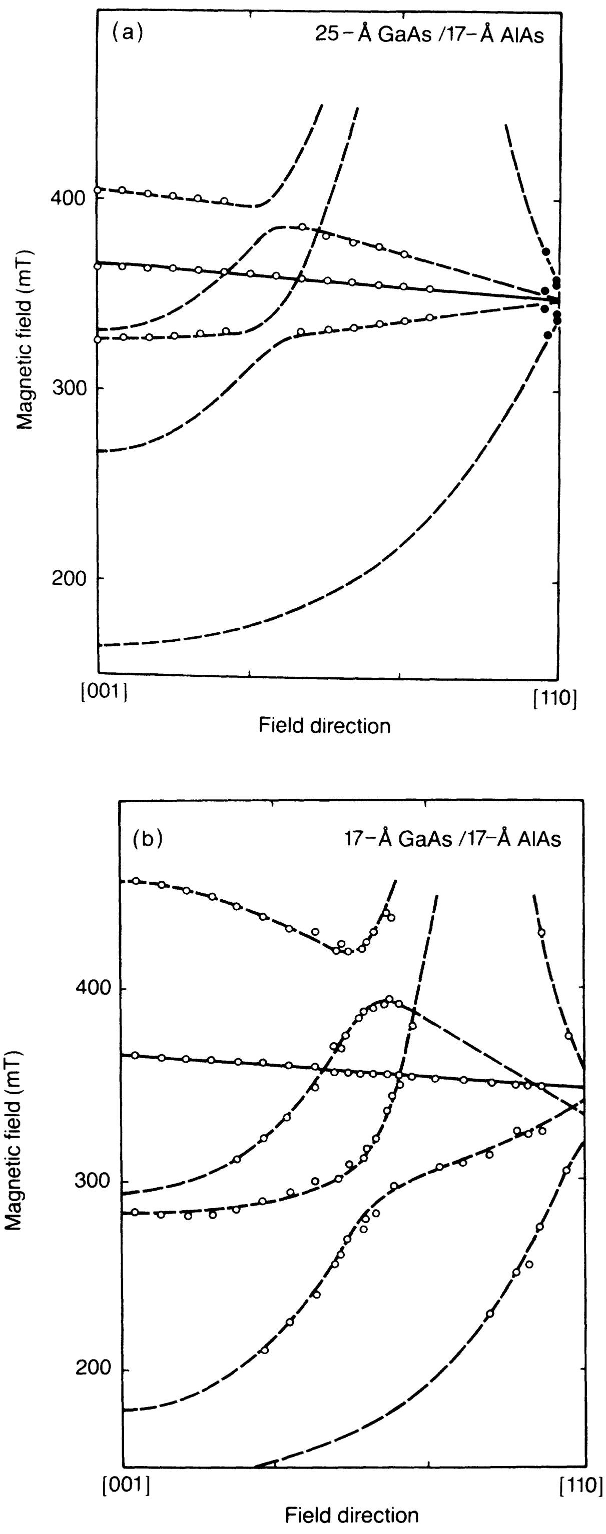

FIG. 6. Rotation diagrams in the (1$\bar{1}$0) plane for (a) the (25 Å GaAs)/(17 Å AlAs) and (b) the (17 Å GaAs)/(17 Å AlAs) sample. The black dots represent data obtained in a different experimental setup and have been corrected for a slight difference in microwave frequency. The solid and dashed lines show the calculated angular dependence of the electron and exciton resonances, respectively, obtained with the parameters given in the Tables I and II.

while the signs for the two classes are opposite. The outer lines cross when the magnetic field is along [100] or [010]. Because the crossing resonance lines have opposite polarity, the resonances of the two classes of excitons should be observed only in the neighborhood of the [110] and [$1\bar{1}0$] axes, which is in accordance with the observations.

ODMR spectra were also studied as a function of the orientation of the magnetic field in the ($1\bar{1}0$) plane. Rotation diagrams are shown in Figs. 6(a) and 6(b). Especially for the (17 Å GaAs)/(17 Å AlAs) sample the angular dependence becomes complicated and extra lines show up. This is a consequence of the spin-spin interaction becoming of comparable magnitude to the microwave energy for the thinnest layer samples. A computer fit was obtained by a direct diagonalization of the spin Hamiltonian (3). For the fits, the spin-spin coupling coefficients were used which were obtained from the ODMR spectra with the field along the principal axes. The remaining fit parameters are the in-plane electron and perpendicular hole g values. Because all transitions observed correspond essentially to electron spin transitions, the hole g value cannot be determined directly. However, for the samples with a relatively large spin-spin splitting, the $g_{h,z}$ value can be deduced from the angle of the magnetic field with respect to the quantum-well axes for which the exciton energy levels cross. These crossings are detected as changes in the intensity of the ODMR lines and by the observation of extra resonance lines in the neighborhood of these crossings. Also, the strong shift to lower and higher fields of the in-plane resonances when the field is rotated out of the quantum-well plane can be used to determine the $g_{h,z}$ value. The fits obtained with the parameters given in Tables I and II are shown in the figure with the solid and dashed lines for the electron and exciton resonances, respectively. The electron and exciton spectra for one sample could in all cases be fitted with the same electron g values. For the 17 Å GaAs sample the hole $g_{h,z}$ value is equal to 2.9 ± 0.1 while for all three 25 Å GaAs samples it amounts to 2.3 ± 0.1. Furthermore, the anticrossing of the resonances in the rotation diagrams were shown to be only compatible with $g_{e,z}$ and $g_{h,z}$ having opposite signs [using the sign conventions of Eq. (3)]. From the fact that the in-plane splittings are due to spin-spin interaction, an upper limit for the $g_{h,x}, g_{h,y}$ values can be obtained. These values are given also in Table II.

IV. DISCUSSION

In a previous publication[8] a detailed analysis was given of the anisotropy of the electron g value for a series of type-II GaAs/AlAs samples with AlAs layer thicknesses between 8 and 200 Å. For the samples with AlAs layers thicker than about 50 Å the spin-spin interaction is no longer resolved in the ODMR spectra and only one resonance is observed. With respect to the sign of the g_e anisotropy, the samples studied were divided into two classes. An anisotropy sign reversal occurred for an AlAs thickness of ~ 55 Å. The change in the sign of the anisotropy could be understood by realizing that the bulk threefold degeneracy of the AlAs X conduction band is lifted in the heterostructures both as a consequence of confinement and of strain. Confinement splits the X valley with momentum vector parallel to the growth direction (labeled X_z) apart from the X valleys with momentum vector in the quantum-well plane (X_x/X_y). The confinement energy for the electrons in the X_z valley, which have a component of momentum along the growth direction, is determined by the longitudinal effective mass, while the confinement for the X_x/X_y valleys is determined by their transverse effective mass which is about six times smaller. Therefore, the X_z valley becomes lowest in energy through the influence of the quantum-well potential. The lattice mismatch strain, however, has an opposite effect on the X valleys, lowering the X_x/X_y valleys and raising the X_z valley. The g value for the electrons on a single ellipsoidal energy surface is anisotropic and differs slightly from the free-electron g value as a result of spin-orbit interaction. From symmetry arguments, the g_e tensor for, e.g., the X_z valley has $g_{e,x} = g_{e,y} \neq g_{e,z}$, where the z axis is the principal axis of the ellipsoid. The experimentally observed change of the sign of the anisotropy for an AlAs thickness of ~ 55 Å is due to the crossover of the X_z and the X_x/X_y valleys and agrees with a calculation of the confinement and strain effect on the X valleys in these structures. Recently, Glaser *et al.*[11] concluded from ODMR measurements on thick epitaxial $Al_xGa_{1-x}As$ layers on GaAs substates that in these structures the X_x/X_y valleys are lowest in energy, which agrees with the result of the ODMR measurements on GaAs/AlAs quantum wells with thick AlAs layers. The samples with the exchange split exciton resonances discussed in this paper all have AlAs layers thinner than 55 Å. Therefore, all these samples show the same axial symmetry along the [001] axis and magnitude of the g_e anisotropy.

The anisotropy of the g value for the holes is much larger than the anisotropy for the electrons, as can be seen from Table II. The perpendicular g_h values are in between 2 and 3 while the in-plane values are smaller than 0.01. This strong anisotropy of the effective hole g value is a consequence of the description of the heavy-hole states with $J_{h,z} = \pm \frac{3}{2}$ by an effective spin $\tilde{S}_h = \frac{1}{2}$. From the spin Hamiltonian (2) it can be seen that the in-plane splittings can only be due to the cubic hole Zeeman interaction terms. The small values of $g_{h,x}$ and $g_{h,y}$ correspond, therefore, to a small q value in a bulk semiconductor. On the other hand, the bulk linear hole Zeeman splitting constant κ, which is about 1.2 for GaAs,[12] corresponds to a $g_{h,z}$ value of 7.2. This bulk value is much larger than the experimentally determined $g_{h,z}$ values of 2.3 and 2.9 for, respectively, the 25 and 17 Å GaAs layer samples.

Spin splittings of type-I excitons have been studied by Ossau *et al.*[13] by magneto-optic spectroscopy. Due to the small electron spin g value of ~ 0.4 for GaAs, the exciton spin splittings are mainly determined by the hole g value. In low fields (< 1 T) the effective hole g value was found to be 1.1, 0.9, and 0.3 for GaAs thicknesses of 240, 180, and 120 Å, respectively. For higher fields the hole spin splitting is strongly nonlinear, as is evident from the sign reversal of the hole g value at 3 T for the 180 Å GaAs well. Assuming that the hole g values are comparable for the type-I and type-II excitons, we can extrapolate the low-field hole g values to 25 and 17 Å GaAs thicknesses, yielding g values in the 1–5 range with an opposite sign. The magnitude and sign of the $g_{h,z}$ value determined from the ODMR spectra and the fact that it is larger for a 17-Å layer than for a 25-Å layer is in accordance with the extrapolation. The nonlinearity and the magnitude of the spin splitting as a function of the magnetic field was explained by Bauer and Ando[14] as being due to valence-band mixing. It is therefore most likely that the large difference of the hole g value determined from the ODMR spectra and the bulk value is also due to these mixing effects. However, a separate calculation for the type-II excitons should be performed to confirm this.

In the type-II quantum wells the spin-spin interaction is found to depend strongly on the thicknesses of the layers. The increase of the coupling for decreasing layer thickness is in qualitative agreement with the expected behavior. The spin-spin interaction can in principle be due to magnetic multipole interactions as well as to exchange. To determine the origin of the spin-spin splittings we consider first the magnetic dipole-dipole interaction. In a point-dipole model the magnitude of c is given by

$$c=\frac{\mu_0 g_e g_h \mu_B^2}{4\pi r^3}\,, \tag{5}$$

where μ_0 is the permeability of vacuum and r the distance between the two point dipoles.[15] For the (14 Å GaAs)/(14 Å AlAs) sample, which has $c_e=34\ \mu$eV, a distance between the point dipoles of 2 Å is found using Eq. (5), i.e., $\frac{1}{3}$ of the lattice constant. Although the point-dipole model is not expected to give an accurate description of the magnetic dipole-dipole splitting of the type-II excitons, the smallness of r compared to the exciton radius, which is in the 100-Å range, makes it quite unlikely that the spin-spin coupling is by magnetic dipole-dipole interaction. Furthermore, the dependence of the spin-spin interaction on the well and barrier thickness is roughly exponential and is not described by an r^3 dependence. Higher multipole interactions would be even smaller. Therefore, the spin-spin interaction is considered to be due to exchange.

Recently, Rejaei Salmassi and Bauer[16] calculated the exchange interaction for type-II excitons in an effective-mass approximation. The exchange interaction was represented by a δ function of the electron and hole coordinates and the exchange splitting was obtained by perturbation theory using the calculated envelope function for the type-II excitons. In Fig. 7 the calculated and experimentally obtained exchange splittings are shown as a function of the layer thicknesses. In the theory the bulk exchange integral is treated as a free parameter. This constant has been obtained from the exchange splitting of the sample with the largest width for which the theory is believed to be most reliable. The trend in the experimental values agrees fairly well with the theory, supporting

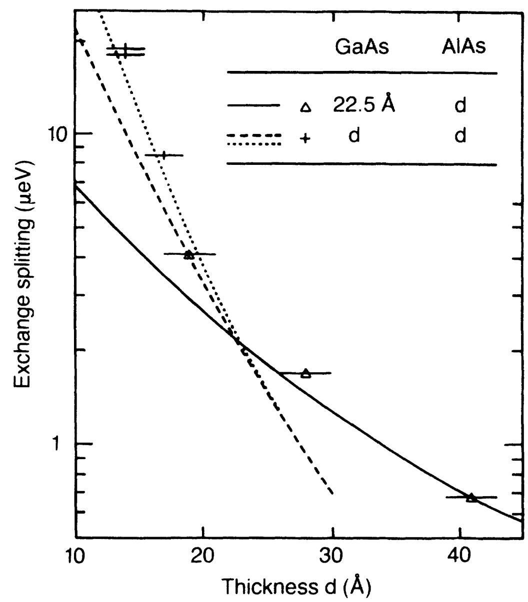

FIG. 7. Exchange splitting between the zero-field radiative and nonradiative levels $(1/2c_z)$ for the type-II excitons as a function of the layer thicknesses. The triangles represent the experimental results for the samples with a GaAs thickness of ~22.5 Å and a varying AlAs thickness; the crosses are for the samples with equal GaAs and AlAs thicknesses. The lines show the theoretical splittings (Ref. 15). The dotted line represents an estimation of the effect of particle tunneling into neighboring layers.

the interpretation that the splittings are due to exchange. The slight deviations for the thinner layer samples are probably due to the effect of tunneling into the neighboring layers and to the nonparabolicity of the X conduction band.

Not only the splitting between the exciton resonance lines but also the width of the lines increases with decreasing thickness of the layers (see Fig. 3). For the (25 Å GaAs/(25 Å AlAs) sample the full width at half maximum (FWHM) is 5 mT, whereas for the (17 Å GaAs)/(17 Å AlAs) it amounts to 60 mT. This is in contrast to the electron resonance, which has a constant width of 4 mT. Because the exchange interaction depends on the separation of the electron and hole forming the exciton, interface roughness can lead to a broadening of the exciton resonances. The width of the exciton lines can be related to these thickness variations by using the dependence of the exchange splitting on the layer thicknesses shown in Fig. 7. With the exception of the (25 Å GaAs)/(42 Å AlAs) sample, all the FWHM values correspond to ~3 Å thickness variations, i.e., 1-monolayer difference in layer thickness. The exciton resonances for the (25 Å GaAs)/(42 Å AlAs) show an extra splitting which is just resolvable. It is unlikely that these extra lines are due to hole transitions because of the symmetrical occurrence with respect to the electron spin resonance. The most likely explanation of the lines is that they are due to excitons localized at different steps at the interface. Indeed, relating the splitting to a thickness variation gives a value of ~6 Å, i.e., 2 monolayers. The fact that the thickness variations of 3 Å in the other samples, which correspond to larger splittings of the resonance lines, are not resolved is probably due to the fact that the roughness of 1 monolayer occurs within the radius of the exciton. According to recent TEM measurements[17] an interface roughness of 1 to 2 monolayers is certainly not unreasonable.

Recently the zero-field levels of the type-II quantum wells were also studied by time-resolved optical spectroscopy by van der Poel *et al.*[18] By exciting the excitons directly with a picosecond pulse into a coherent superposition of eigenstates, they were able to detect quantum beats in the exciton luminescence. The beat frequency, which corresponds directly to the splitting between the radiative levels, was 80 MHz (0.3 μeV) for the (25 Å GaAs)/(42 Å AlAs) and 180 MHz (0.7 μeV) for the (25 Å GaAs)/(25 Å AlAs) sample. These splittings are in good agreement with the zero-field ODMR results, assuming that the largest splitting is between the radiative levels, i.e., that c_x and c_y have the same sign. In the previous section the same conclusion was drawn to explain the polarity of the in-plane ODMR signals of the two classes of excitons.

The analysis of the ODMR spectra revealed that besides the splitting of the radiative levels, there is also an in-plane anisotropy. This implies that the exciton symmetry is lower than D_{2d}. To explain the doubling of the peaks in the in-plane spectra we had to assume that there are two classes of excitons with their x and y axes interchanged. However, if these two classes differed only in their x and y axis orientation, the ODMR spectra should be the same for the [110] and [1$\bar{1}$0] direction. With respect to the splitting pattern this is indeed observed but with respect to the relative intensity for the various lines there is clearly a difference for these two orientations (Figs. 1 and 5). This shows that the overall symmetry is still lower than D_{2d}. The observation by van der Poel *et al.*[18] of beats not only in the linear but also in the circular polarization led them to a similar conclusion with respect to the overall symmetry.

Because the electron and hole forming the exciton are situated on either side of the GaAs/AlAs interface, the interface structure should be responsible for these effects. The symmetry at the interface is lowered extrinsically by the steps at the interface which are due to the misorientation of the substrate as well as to the MBE growth mechanism. Reflection high-energy electron diffraction (RHEED) oscillation studies during MBE growth have shown that the step density is different for the [110] and [1$\bar{1}$0] direction. This has been interpreted as being due to islands elongated in one of these directions.[19] Furthermore, there is an intrinsic lower symmetry because the bonds at the interface are either along a [110] or [1$\bar{1}$0] direction.[20] If the symmetry of the excitons is lowered by the substrate misorientation, one of the principal in-plane axes is expected to correspond to the direction of the misorientation. From the experiments it is clear that the principal in-plane axes for all the samples correspond to the [110] and [1$\bar{1}$0] quantum-well axes. Because it is unlikely that the direction of the substrate misorientation is exactly along the principal in-plane axes for all the samples, a symmetry lowering by the substrate misorientation becomes less likely. Whether the MBE growth mechanism or the bond direction determines the exciton symmetry cannot be concluded from the present experiments. A comparison of the ODMR spectra of MBE and metalorganic chemical vapor deposition (MOCVD) samples, as well as samples grown with and without growth interruption, might be useful to reveal the origin of the symmetry lowering.

For each hole, excitons can be formed with an electron on either side of the well. These two excitons are related by the D_{2d} symmetry operations. The experimental finding that for the two classes of excitons $c_x^{\mathrm{I}} = -c_y^{\mathrm{II}}$ and $c_y^{\mathrm{I}} = -c_x^{\mathrm{II}}$, i.e., that the splitting patterns for the two classes are related by D_{2d} symmetry operations, makes an identification of the two classes of excitons with the excitons on the GaAs/AlAs and AlAs/GaAs interface quite likely. Although there is an equivalence for the two principal in-plane axes with respect to the splitting pattern, this symmetry is broken when the intensities of the resonance lines in zero-field and with an in-plane magnetic field are considered. This is most likely related to the different microscopic structure of the GaAs/AlAs and AlAs/GaAs interface. Tanaka *et al.*[21] have shown that the step density can be largely different for these two interfaces as a consequence of the different diffusion lengths of Ga and Al atoms during MBE growth. The different roughness of the GaAs/AlAs and AlAs/GaAs interface can, for instance, result in different populations or spin relaxations of the two classes of excitons which would account for the observed inequivalence of these two classes.

V. CONCLUSIONS

The fine structure of excitons in type-II GaAs/AlAs quantum wells with varying GaAs and AlAs thicknesses has been studied by ODMR. The spectra were analyzed using the spin-Hamiltonian formalism and the results are expressed by the electron and hole g values and the electron-hole spin-spin coupling constants. To obtain these parameters the ODMR spectra were studied in zero-field as well as in a finite magnetic field, while the dependence of the resonance fields on the direction of the magnetic field with respect to the quantum-well axes was also investigated. The anisotropy of the electron spin g values is in accordance with a lifting of the threefold degeneracy of the AlAs X conduction band by the quantum-well potential giving the X_z valleys the lowest energy in the samples studied. The different magnitude of the hole g value compared to the bulk and the dependence on the thickness of the GaAs layer is probably due to valence-band mixing in the quantum wells. An accurate determination of the exciton exchange coupling for quantum wells with varying GaAs and AlAs thicknesses is obtained. The trend for the exchange interaction agrees with the effective-mass calculation by Rejaei Salmassi and Bauer.[16] The width of the exciton resonances corresponds to an interface roughness of 1 to 2 monolayers with variations of 1 monolayer occurring within the exciton radius of ~100 Å. Furthermore, the actual symmetry of the excitons is lower than D_{2d} and there are two classes of excitons with their principal [110] and [1$\bar{1}$0] axes interchanged. Because the fine structure of the excitons is related to the structure of the GaAs/AlAs interface, it should be possible to use the ODMR technique to obtain information on the interfaces in GaAs/AlAs quantum wells.

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