Excitonic spectrum of [111] GaAs/$Ga_xAl_{1-x}As$ quantum wells

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We have studied the magneto-optical properties of GaAs/$Ga_xAl_{1-x}As$ quantum wells grown along the [111] crystallographic direction. The excitonic spectrum has been obtained by means of photoluminescence excitation measurements in the presence of an external magnetic field. From the analysis of the data we extract the binding energies and the excitonic reduced effective masses as a function of well width. A study of the polarization of the emission, exciting with circularly polarized light, yields information about the spin relaxation and its dependence on magnetic-field strength. The results are compared with available calculations and with those obtained in samples grown along the [001] direction.

I. INTRODUCTION

Most of the studies on III-V semiconductor quantum wells (QW's) have been performed on samples grown on [001]-oriented substrates, mainly due to the superior crystal quality which can be attained for this direction. However, it has become possible to grow heterostructures with the quantization axis along a variety of crystallographic directions.[1-17] Although it is difficult to prepare high-quality QW's on non-[001]-oriented substrates, the quality of these QW's has been dramatically improved by a slight misorientation of the substrates. The interest of growing in different directions is due to the expectation that the QW properties will depend on the growth axis as a result of the anisotropy of the valence-band structure in bulk materials. The complexity of the valence band, especially its anisotropy, offers an extra degree of freedom to tune the optical properties and for the design of electro-optical devices.

Several works have appeared recently in the literature dedicated to the electrical,[6,7] optical,[8-15] and vibrational[16,17] properties of GaAs/$Ga_xAl_{1-x}As$ QW's grown on different crystallographic directions. These studies find differences in the band structure depending on the growth direction and suggest possible improvements of the electronic properties of QW's with the quantization axis along the [111] direction. Different groups have confirmed, by optical experiments, that the confinement mass of the heavy hole ($m^*_{h\perp}$) in [111]-oriented GaAs/$Ga_xAl_{1-x}As$ QW's is a factor of 2–2.6 larger than in [001]-oriented ones.[4,8,10-13] The values of $m^*_{h\perp}$ range from 0.7 to 0.9. As a consequence of the heavier mass, the subbands are more closely spaced and the relative ordering of the heavy- (hh) and light-hole (lh) subbands changes for certain well widths.[18] Hayakawa *et al.* reported on an enhancement of the optical-transition rates and a decrease in the threshold current densities for [111]-oriented QW lasers relative to [001]-oriented ones.[12] An electric-field-induced shift of the ground-state heavy-hole exciton [$h_1(1s)$]~30% larger for [111] QW's than for [001] wells has been found, due to the larger confinement mass of the hh subband along the [111] direction.[13] This result could be used to improve the performance in optical devices based on the Stark effect. It has been also shown experimentally that the electric-field-induced change in birefringence in [111] GaAs/$Ga_xAl_{1-x}As$ QW's is enhanced over that of [001] QW's.[19] An improvement of the peak-to-valley ratio by a factor of 2 for AlAs/GaAs/AlAs double-barrier heterostructures grown along the [111] crystal axis, compared to that of samples grown in the [001] orientation, has also been established.[20] It should also be mentioned that in the case of strained-layer superlattices (SL's) grown along the [111] axis, as, for example, $Ga_xIn_{1-x}As/Al_xIn_{1-x}As$, additional properties not present in strained [100] SL's are found. The most striking one is the appearance of strain-induced polarization fields, which causes nonlinear optical response of these SL's.[21,22]

We have used high-resolution photoluminescence-excitation (PLE) spectroscopy to study the pseudoabsorption of [111]-oriented GaAs/$Ga_xAl_{1-x}As$ QW's in the presence of an external magnetic field. Under the

influence of a magnetic field the exciton continuum splits into excited states; the observation of the diamagnetic shifts of the ground and excited states of the excitons and the use of a two-dimensional (2D) hydrogenic model[23] to fit the magnetointerband transitions allows the determination of the binding energies and the reduced effective masses of the excitons.[24] Additionally, the magnetic-field-induced lifting of the Kramers degeneracy, combined with the use of circularly polarized light, allows the selection of excitons associated with different spin orientation of the holes. An analysis of the polarization of the emission gives further information on the spin relaxation of photogenerated carriers[25–27] and on the mixing of different excitonic states.

This paper is organized as follows. After a brief description of the experimental details (Sec. II), we present photoluminescence (PL) and PLE spectra in the presence of a magnetic field (Sec. III). The binding energies and effective masses are discussed in Sec. IV. In Sec. V we examine the polarization dependence of the spectra. Section VI contains the summary.

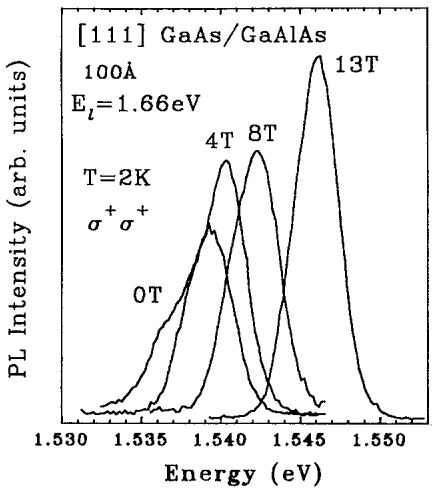

FIG. 1. Photoluminescence spectra for a 100-Å wide GaAs/$Ga_xAl_{1-x}As$ QW grown on the [111] direction at different magnetic fields. The spectra were obtained at 2 K, exciting at 1.66 eV with σ^+ circularly polarized light, detecting only the right-handed polarized emission.

II. EXPERIMENTAL DETAILS

The samples studied here were grown by molecular-beam epitaxy on [111]*B* semi-insulating GaAs substrates, with crystal orientation tilted 3° to improve their optical quality.[3] A 1-μm GaAs buffer layer was followed by 475 Å of $Ga_{1-x}Al_xAs$ and five identical GaAs QW's separated by 200-Å $Ga_{1-x}Al_xAs$ barriers with $x=0.3$. The samples were capped by 500 Å of $Ga_{1-x}Al_xAs$. All the layers were nominally undoped. Four different samples, with well thicknesses of 60, 75, 100, and 130 Å, were investigated. Their width was determined by fitting the hh and lh excitonic energies, using a Kronig-Penney model. For the calculations we have used the measured binding energies (see Sec. IV) and the effective-mass parameters and band discontinuity from Ref. 10. We have also measured the pseudoabsorption of a [001]-oriented GaAs/$Ga_{0.7}Al_{0.3}As$ QW of 100 Å for comparison purposes.

The samples were excited with the light from a LD700 and a Rhodamine 6G dye laser, pumped by Kr^+ and Ar^+ lasers, respectively. The power density was kept below 0.1 W cm^{-2}. The incident light was circularly polarized by means of an achromatic $\lambda/4$ plate. The specimens were immersed in a liquid-He bath cryostat within a standard-coil superconducting magnet. Magnetic fields, up to 13.5 T, were applied in Faraday configuration. Their emission was dispersed with a double-grating monochromator and the PL intensity was measured with a cooled GaAs photomultiplier coupled to a photon-counting system. The PL was analyzed into its σ^+ and σ^- components using a combination of an achromatic $\lambda/4$ plate and a linear polarizer.

III. RESULTS

Photoluminescence spectra of the 100-Å sample, excited with σ^+ polarized light and analyzed into their σ^+ component, are depicted in Fig. 1 for four different magnetic fields. The PL was excited at 1.66 eV, below the $Ga_xAl_{1-x}As$ band gap. At zero field, the PL is dominated by excitonic emission, with the presence of shoulder at lower energies. The typical quadratic diamagnetic shift of the h_1 exciton is clearly observed. It amounts to 6 meV at 13 T. The full width at half maximum (FWHM) diminishes from 4.6 meV at 0 T to 3.3 meV at 13 T. This decrease is due to the quenching of the low energy band of the PL with increasing magnetic field. For the other samples the FWHM's at 0 T are 7 meV (60 Å), 5.4 meV (75 Å), and 2.5 meV (130 Å). These values of the FWHM's, which are a factor of ~ 1.5 better than previously reported widths,[28] indicate the high quality of our samples. The nonmonotonic behavior of the PL intensities with magnetic field, seen in Fig. 1, can be related to the changes in the absorption coefficient at 1.66 eV for different magnetic fields. Additionally, the PL strength also depends on the polarization configuration, not only because of the changes in absorption but also due to the relaxation processes.

Photoluminescence excitation spectra for the thinnest QW (60 Å), obtained in the $\sigma^+\sigma^+$ configuration, are shown in Fig. 2 at three different magnetic fields. The spectra are displaced vertically, for clarity, by the amount shown with the tics in the vertical axis. In the measurements the intensity was detected at the peak of the PL, which lies ~ 7 meV below the lowest transition observed in the PLE spectra. At zero field, the pseudoabsorption spectrum shows only two peaks, which correspond to the ground-state h_1 and l_1 excitons. With increasing magnetic field a series of new structures appear in the spectra, which are associated to the excited states of the h_1 exciton. The excited states of the l_1 exciton are weaker and its observation is hindered by the relatively large width of the excited h_1 states. At 8 T the ground-state light-hole exciton, $l_1(1s)$, is hidden below $h_1(2s)$.

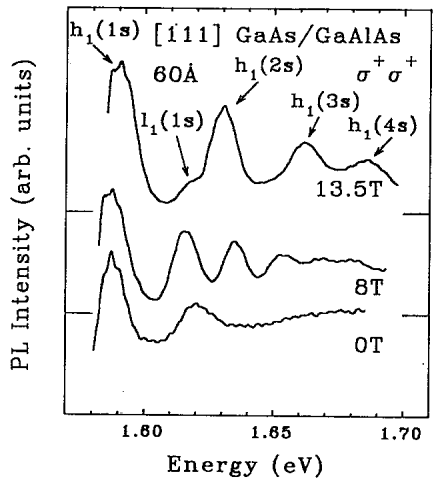

FIG. 2. Photoluminescence excitation spectra of a 60-Å-wide [111]-oriented GaAs/$Ga_xAl_{1-x}As$ QW at three different magnetic fields in $\sigma^+\sigma^+$ configuration. The light was detected at the peak of the PL. The ground heavy- and light-hole excitons, $h_1(1s)$ and $l_1(1s)$, and the excited states of h_1 are marked by arrows.

Both states belong to different symmetries and therefore they do not couple,[29,30] as borne out by our experiments. As it has been shown before,[24] the spectra of thin QW's demonstrate the "hydrogeniclike" behavior of quasi-two-dimensional excitons, where most of the complications present in wider wells, due to the complexity of the valence-band structure, can be avoided.

The increased richness of the spectra for wider wells is demonstrated in Fig. 3, where several PLE runs obtained in the $\sigma^+\sigma^+$ configuration are shown for the thickest sample (130 Å). The 0-T spectrum, which was recorded at the low-energy tail of the PL, displays three structures.

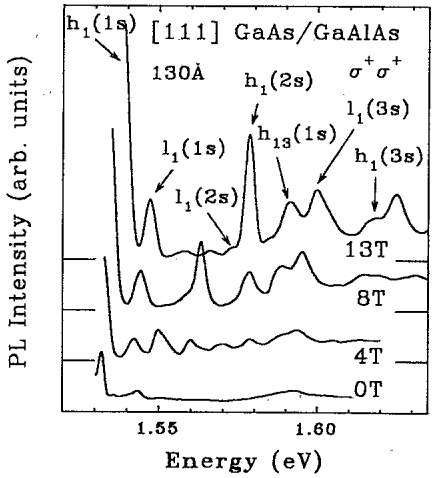

FIG. 3. Photoluminescence excitation spectra of a 130-Å-wide [111]-oriented GaAs/$Ga_xAl_{1-x}As$ QW at different magnetic fields in $\sigma^+\sigma^+$ configuration. The light was detected at the low-energy side of the PL for the 0-T spectrum and at the peak of the PL for the rest of the spectra.

They correspond, in increasing energy order, to the ground state of the first hh exciton, $h_1(1s)$, first lh exciton, $l_1(1s)$, and the weakly forbidden $h_{13}(1s)$ exciton (the first subindex denotes electrons and the second holes). The rest of the spectra were recorded at the peak of the PL, which for this sample shows a Stokes shift <1 meV with respect to the PLE. With increasing field there is a reduction of the exciton radius, which increases the oscillator strength of the excited states and therefore favors its observation. Up to the highest field shown in the figure, the intensity of $h_1(2s)$ increases monotonically with increasing field. However, this is not the case for other states, as, for example, $h_1(3s)$ and $l_1(3s)$, since many interactions lead to a complicated behavior of their intensities. By analogy with previous experiments and identifications based on a theory of excitonic coupling,[30] we attribute the weak structures seen at 13 T between $l_1(1s)$ and $l_1(2s)$ to forbidden excitonic transitions.

For comparison, we show in Figs. 4(a) and 4(b) PLE spectra at different magnetic fields for two QW's of 100 Å width grown along the [111] and [001] direction, respectively. The higher crystal quality of the [001] QW is reflected in the sharpness of the excitonic peaks. The energy of the ground-state $h_1(1s)$ exciton is slightly smaller (~ 5 meV) in the case of the [111]-oriented QW, due to the larger confinement effective mass in this crystallographic direction. The change in the confinement mass is also patent in the observation of the $h_{13}(1s)$ exciton [peak at 1.625 eV at 4 T in Fig. 4(a)] in the [111]-oriented QW, while it lies at higher energy, 1.635 eV, in the [001] QW (not shown). However, the position of the $l_1(1s)$ exciton differs only by ~ 1 meV between both samples, revealing the isotropy in the dispersion of the lh band. The second hh subband, for this QW thickness, is predicted to lie above the first lh subband in [001] QW's, while this order should be transposed in [111] oriented ones.[18] This reversal is clearly visualized in the 0-T spectra of Fig. 4(a): the peak at 1.55 eV, lying between $h_1(1s)$ and

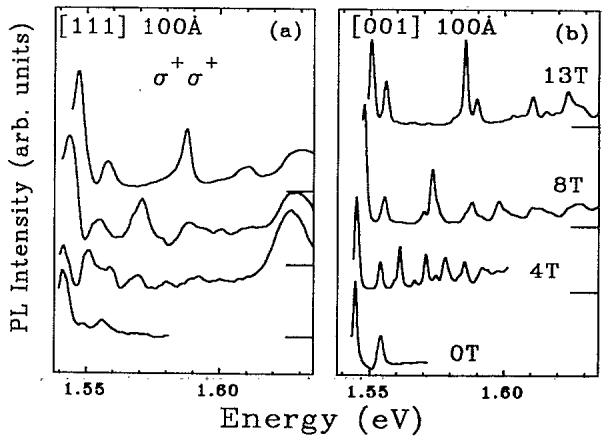

FIG. 4. PLE spectra for 100-Å-wide GaAs/$Ga_xAl_{1-x}As$ QW's: (a) grown along the [111] direction; (b) grown along the [001] crystallographic direction. The spectra were recorded in $\sigma^+\sigma^+$ configuration, and are displaced horizontally for clarity by the amount shown by the tics. Note the higher quality of the [001] oriented sample in the sharpness of the excitonic peaks.

$l_1(1s)$, corresponds to the first electron to second hh excitonic transition, h_{12}. The presence of this forbidden transition must be related to band-mixing effects.[29] The absence of h_{12} in the [001] QW indicates that these effects are less important, for this well width, in the [001] direction. At nonzero magnetic fields, the spectra present similar structures, excepting that the relative ordering of the h_1 and l_1 excited states is reversed in some cases [compare heavy-light doublet at 1.585–1.595 eV in Fig. 4(b) with that at 1.575–1.59 eV in Fig. 4(a) at 13 T, the identification of the heavy-light character of the excitons will be discussed below], and that the excited excitonic states are better resolved in Fig. 4(b) due to the higher crystal quality. An additional dissimilarity lies in the diamagnetic shift of the excitons, which is larger for [111] QW's compared to that of [001] QW's: the term splitting $h_1(2s)-h_1(1s)$ amounts to 40 meV (35 meV) at 13 T for the [111] ([001]) QW. This difference can be related to the change in the in-plane effective mass for different crystallographic directions, as will be discussed in Sec. IV.

The excitation with circularly polarized light, which selects excitons associated to holes with antiparallel spin components, enables the resolution of closely lying states. Additional information can be obtained by analyzing the polarization of the emission, as demonstrated in Fig. 5. The uppermost curve shows a PLE spectrum of the 100-Å QW at 6 T for σ^- excitation. The two lowest curves have been recorded analyzing the PL into left- and right-handed polarizations, respectively. The triplet in the 1.55–1.565-eV range, corresponding in increasing energy order to h_{12}, $l_1(1s)$, and $h_1(2s)$ excitons, is only resolved in the $\sigma^-\sigma^-$ configuration. In this figure is also clearly seen the effect of the selection rules: $h_1(1s)$ is a factor

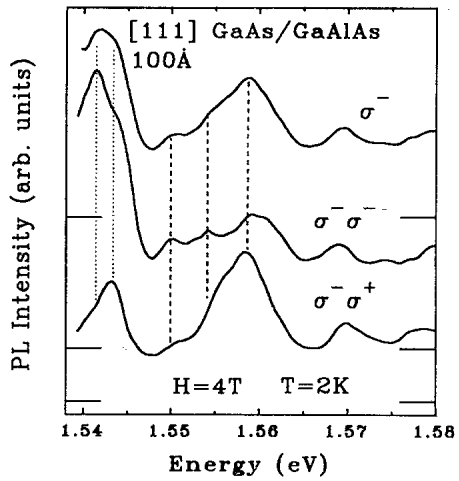

FIG. 5. PLE spectra at 4 T of a 100-Å wide [111] oriented $GaAs/Ga_xAl_{1-x}As$ QW excited with σ^--polarized light. In the two lowest spectra the emission at $h_1(1s)$ is analyzed into its σ^+ and σ^- components, while in the topmost spectrum both polarizations are detected. Note that only in $\sigma^-\sigma^-$ the triplet, h_{12}, $l_1(1s)$ and $h_1(2s)$, in the 1.55–1.56-eV range is fully resolved. The dotted lines in the $h_1(1s)$ exciton emphasize its splitting.

~ 2.5 smaller in $\sigma^-\sigma^+$ than in the parallel configuration (parallel refers either to $\sigma^-\sigma^-$ or $\sigma^+\sigma^+$). This is expected from selections rules, since the heavy-hole exciton, derived mainly from $|J=\frac{3}{2}, J_z=\frac{3}{2}\rangle$ valence-band states, should be ideally observed only in parallel polarizations. A similar effect is also observed in the midst component of the triplet, $l_1(1s)$, which should have a larger strength in antiparallel polarizations, as borne out from our experiments. An additional fact is seen in the $h_1(1s)$ exciton when the emitted light is analyzed into its circularly polarized components. The peak in the σ^+ emission lies ~ 2 meV above the maximum in the σ^- one. This splitting is also observed at 0 T and may be originated from exchange interaction between excitons, as will be discussed in Sec. V.

IV. BINDING ENERGIES AND EFFECTIVE MASSES

The knowledge of the exciton binding energies in semiconductor QW's is one of the most important issues related to the effects of quantum confinement. This information is easily attained experimentally, in high-quality samples, from the term splitting between the ground and first excited state of the excitons.[11,31,32] Binding energies have been also obtained from magnetointerband spectroscopy, which additionally gives information on reduced effective masses.[24,33–35] The former information is basically obtained from the determination of the term splitting, $h_1(2s)$-$h_1(1s)$, while the latter is related to the slope of the diamagnetic shift of the excitons. The use of a two-dimensional hydrogenic model to fit the magnetointerband transitions incorporates both parameters to describe the results,[23,24,35] and therefore avoid the inaccuracies of the nonlinear zero-field extrapolations which have been performed in the past.

The fan chart of the pseudoabsorption peaks, exciting with σ^- polarized light, for a [111]-oriented 100-Å QW are depicted in Fig. 6. The peaks at 0 T correspond to $h_1(1s)$, h_{12}, and $l_1(1s)$, in increasing energy order. As the magnetic field is increased the ns excited states become observable. Two sets of transitions can be clearly distinguished. The ground and excited states of the heavy-hole exciton, $h_1(ns), n=1$ to 3, are shown as solid circles, while the corresponding light-hole excitons, $l_1(ns)$ are depicted as open circles. The resolution of heavy and light excited states is facilitated by the analysis of the polarization of the emitted light (see Fig. 5). The ground states exhibit the typical behavior in a magnetic field, with only a very weak magnetic-field dependence. The higher excited states show an almost linear dependence at high fields.

The experimental results are fitted using a 2D hydrogeniclike excitonic model, extending the analytical expressions given in Ref. 23 to the case of finite hole mass. The excitonic energies can be written as

$$E_{n,m}=E_g^{2D}+\frac{\mathrm{Ry}^*}{4}\xi_{n,m}(z)\,, \tag{1}$$

where E_g^{2D} is the energy gap, taking into account confinement effects, Ry* is the effective Rydberg or binding energy, and n,m are the principal and the angular

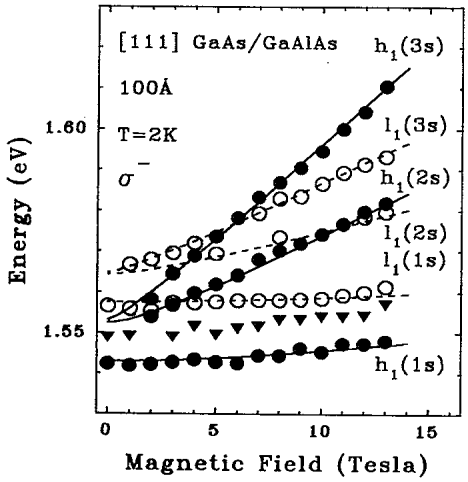

FIG. 6. Energies vs magnetic field for σ^- excitation of the ground and excited state heavy-hole (solid points) and light-hole (open points) excitons for a 100-Å, [111]-oriented QW. The triangles depict the forbidden h_{12} exciton. The full (dashed) lines show the result of the fits with a two-dimensional excitonic model for the heavy-hole (light-hole) excitons (see text).

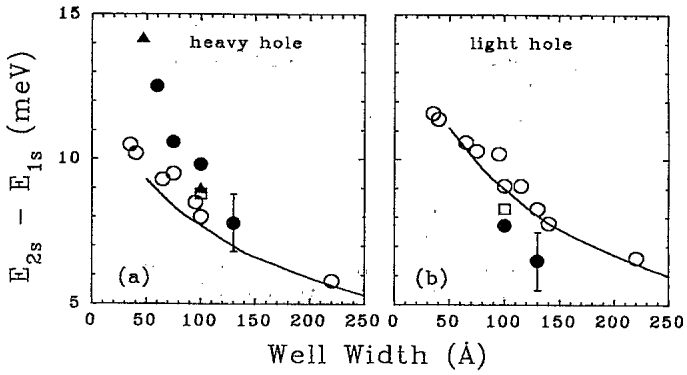

FIG. 7. Term splitting of the (a) heavy-hole and (b) light-hole excitons as a function of well width. The full symbols correspond to [111]-oriented QW's, while the lines and open circles depict results in [001]-oriented QW's compiled in Ref. 32. The full dots and open squares show the present results, and the triangles are obtained from Ref. 11.

quantum numbers, respectively. $\zeta_{n,m}(z)$ is a two-point Padé approximant, which has the following expression:

$$\zeta_{n,m}=\frac{P_{n,m}}{Q_{n,m}}=\frac{p_{n,m}^{(0)}+p_{n,m}^{(1)}z+p_{n,m}^{(2)}z^2+\cdots}{q_{n,m}^{(0)}+q_{n,m}^{(1)}z+q_{n,m}^{(2)}z^2+\cdots}, \quad (2)$$

where $z=\gamma^{1/2}$, and γ is the dimensionless quantity $2\hbar\omega_c^r/\mathrm{Ry}^*$. The cyclotron frequency is $\omega_c^r=eH/m_r^*$, where m_r^* is the reduced effective mass of the exciton.

The coefficients $p_{n,m}$ and $q_{n,m}$ in Eq. (2) are taken from Table V of Ref. 23. The Marquardt-Levenberg algorithm was used to fit simultaneously the ground and excited states of the excitons with three parameters: energy gap (E_g^{2D}), binding energy (Ry*) and reduced effective mass (m_r^*). The heavy- and light-hole fans were fitted separately. The results of the fit are shown in Fig. 6 for the hh and lh excitons as solid and dashed lines, respectively.

For the comparison of the binding energies of the excitons between different sources from the literature, it must be taken into account the procedure used to extract this information from the experiments. It has been pointed out[32] that the binding energies extracted from magneto-optical experiments disagree with those obtained from the direct observation of the term splitting of the excitons, especially when nonlinear extrapolations from large magnetic fields to zero field are needed in the magnetooptical data. However, the agreement between both determinations improves considerably when an adequate model is used to describe the excitonic transitions in the presence of a magnetic field.[32,34,36] We present in Figs. 7(a) and 7(b) the deduced values of the $2s$-$1s$ splitting for the hh and lh excitons, respectively, and compare them with the most reliable data found in the literature. The closed (open) symbols correspond to [111] ([001]) oriented QW's. The full circles and the squares depict the results from our experiments. The open circles were obtained from Koteles and Chi,[32] who also compiled the data obtained by Dawson *et al.*[31] and by Miller *et al.*[37] (shown as a line). The triangles were obtained from the direct observation of the $2s$ excited state in high-quality samples in PLE measurements by Hayakawa and co-workers.[11] These authors concluded, from a comparison with data of the term splitting from the literature, that the binding energy of the hh exciton is ~10% larger in [111]-oriented QW's than that in [001]-oriented ones. We also find that the binding energies of the hh exciton are larger in [111] QW's than those in [001]-oriented ones, especially for the narrower wells. However, theoretical calculations show that the binding energies of the hh excitons do not depend significantly on the orientation of the quantum well in the crystalline lattice, and even predict slightly smaller binding energies for [111] QW's compared to [001]-oriented ones.[9,38]

We believe that our comparison with the data for [001] QW's is meaningful, principally taken into account that our value of the term splitting for the [001]-oriented 100-Å QW agrees, within experimental error bar, with the other results from the literature. The results of Miller *et al.*[37] are somehow low as compared with other data; this may be due to the ambiguity in determining the position of the first excited state in samples of not very high quality.

In [001]-oriented QW's, most of the experimental results find larger binding energies for the lh excitons than those for the hh ones.[32] The calculations predict the same behavior, as well as larger binding energies in the [111] direction than in the [001] one.[9,38] However, we find the opposite trend in our experiments for the two widest QW's, whose quality allows the observation of the lh fans. We have obtained for the lh excitons binding energies ~20% smaller than those of the hh excitons. For the 100-Å wide QW's, the binding energies are the same, within experimental error, for both crystallographic orientations. Finally, we should mention that in a very-high-quality QW of 160 Å the term splitting of h_1 was found to be slightly larger than that of the l_1 exciton,[39]

and also that Maan and co-workers[33] have reported larger binding energies for the hh excitons than for the lh ones.

Let us turn now to the effective masses in [111] oriented QW's. There is a general agreement on the increase of the confinement hh effective masses in [111] QW's compared to those of [001]-oriented wells.[4,8,10–13] Nevertheless, there is a discrepancy between theoretical and experimental results concerning in-plane effective masses. Some experiments are interpreted in terms of an increase of the in-plane masses for [111] oriented QW's,[12] while the calculations of the valence-band structure show that, for the same well width, the effective mass for the first subband in [111]-oriented QW's is substantially smaller than that in the [001]-oriented wells.[18,38]

We have obtained for the h_1 exciton in [111]-oriented QW's a value of the reduced effective mass (m_r^*), independent of the well thickness within error bar, of $0.053m_0$ (± 0.003). For the [001]-oriented 100-Å QW the corresponding value is $m_r^*=0.060m_0$ (± 0.003). We have attained for the lh reduced effective mass $0.08m_0$ (± 0.02) independently of well width and orientation; this value of the reduced effective mass yields a negative, "electronlike," mass for the lh subband. The masses in [001] QW's are in reasonable agreement with the results of Tarucha *et al.*,[40] who have obtained reduced effective masses amounting to $0.062m_0$ and $0.12m_0$ (± 0.3) for the hh and lh excitons, respectively. Our results for the hh reduced masses are in agreement with the calculations and also support the interpretation of Houng, Chang, and Wang[18] of the reduction in the threshold current density in laser structures reported in the experiments.[12] The smaller in-plane effective mass of the hh subband in [111] QW's compared to that of [001] QW's may account for the lower threshold, since it reduces the carrier density needed for inversion population.[18]

Kajikawa *et al.*[14] have reported, from a comparison between the peak intensities in photocurrent spectra and calculated oscillator strengths, that the reduced mass of the hh exciton seems to be heavier than that of the lh exciton in [111]-oriented QW's. They find for the ratio of hh to lh excitonic reduced masses a value of 1.1 (0.8) for [111] ([001])-oriented QW's. However, from our measurements in the 100-Å wide [111] and [001] QW's we obtain a ratio of 0.59(± 0.05) and 0.76(± 0.03), respectively. Taking into account that the lh band is isotropic, as also borne out from our experiments, our results for the ratio of reduced effective masses are in agreement with the predicted reduction of the in-plane hh effective masses in [111] QW's.[18,38] Furthermore, this finding conforms with the general result of $\mathbf{k}\cdot\mathbf{p}$ theory, which predicts that the holes which are heavy (light) along the growth direction, become light (heavy) in the QW plane.[41]

Let us finally comment on the relation between the reduced effective masses and the binding energies. In a simple hydrogenic model, a heavier reduced effective mass implies a larger binding energy. However, in our experiments we find larger binding energies for the hh excitons than those for the lh ones while the reduced masses are larger for the lh excitons. We believe that the discrepancy between the experiments and the simplified theory is due to the complicated valence-band structure in QW's (Refs. 42 and 43) and the consequent excitonic mixing.[29] In a rigorous theory, which is needed for a quantitative description of excitonic states in QW's, the hh and lh excitons cannot be treated separately.[29]

V. POLARIZATION EFFECTS

Optical orientation methods, which allow the excitation of states with a preferential spin orientation, using selective optical excitation with circularly polarized light, are very powerful for investigating processes in semiconductors.[44] The optical orientation manifest itself in a polarization of the photoluminescence. At zero magnetic field, the degree of polarization, $\mathcal{P}$, for one of the exciting helicities, is defined as the fractional difference of the PL intensities of two circular polarizations σ^+ and σ^- at a given energy, as a function of the excitation energy: i.e., for σ^+ excitation, $\mathcal{P}=(I^+-I^-)/(I^++I^-)$. Optical pumping experiments allow the identification of fine structure in the absorption spectrum, and they are useful for identification of hh and lh transitions in QW's, since they have opposite polarizations.[45]

Let us consider first polarization effects in the presence of a magnetic field exciting above the hh exciton. Recent PLE experiments under high magnetic fields, using circularly polarized light, have shown that the relaxation time of the magnetic moment of the electrons is much longer than the recombination time and that the magnetic moment is conserved in the recombination as well as during the thermalization process from the excited states.[25] From these experiments, and the temperature dependence of the spin relaxation,[46] it has been proposed that exchange interaction between electrons and holes could be the dominant spin-relaxation mechanism in undoped QW's. The sign of the PL polarization observed in these experiments for the different Landau levels has been explained by calculations of the relaxation processes of photoexcited electrons and holes.[47]

We observe a similar behavior in our [001] QW. Figure 8(a) depicts PLE spectra of this sample in the spectral region of the $l_1(1s)$ and $h_1(2s)$ excitons obtained with σ^- and σ^+ excitation at 12 T. In this QW of comparatively high quality (the Stokes shift between h_1 in PL and PLE amounts to 1.5 meV), the PL for each polarization consists of two peaks [see Fig. 8(b)]. The origin of this doublet is still a matter of controversy and it has been profusely discussed in Ref. 26. One of the possible origins could be related with exchange interaction, which could also be responsible for the splitting of the hh exciton in the [111]-oriented 100-Å-wide sample observed in PLE (see Fig. 5). At large magnetic fields, the emission is split in two components with opposite polarization [I_A and I_B, solid and dashed lines in Fig. 8(b), which correspond to $h_1(1s)\downarrow$ and $h_1(1s)\uparrow$ with σ^- and σ^+ polarizations, respectively]. The splitting between the lowest components of the two split heavy-hole luminescence peaks amounts to 1.4 meV at 12 T. The fact that I_B is also seen in emission indicates that the relaxation time to the lowest state is comparable to the radiative recombination time.[26] The intensities of the two luminescence bands de-

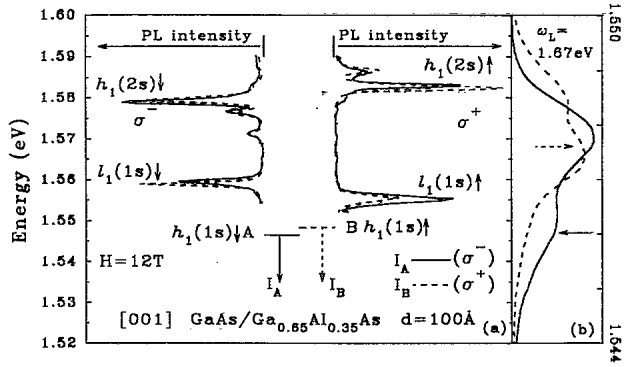

FIG. 8. (a) PLE spectra in the spectral region of the ground-state light-hole exciton and the first excited state heavy-hole exciton for σ^- (left) and σ^+ (right) polarized exciting light at 12 T. The sample was grown on the [001] direction with a QW width of 100 Å. The solid lines correspond to spectra detected at $h_1(1s)\downarrow$, (A), which emits σ^--polarized light. The dashed lines correspond to emission of $h_1(1s)\uparrow$ (B), which is σ^+ polarized. (b) PL spectra of the two components of the heavy-hole spin-split ground states: (A), (solid line) and (B), (dashed line). The spectra were excited at 1.67 eV. The arrows show the energy used for the detection of the PLE spectra shown in the left panel.

pend strongly on which state is pumped, as can be clearly seen in Fig. 8(a), where the detection of I_A and I_B has been done at the points marked with arrows in the PL. These changes of the intensities with energy and helicity of the exciting light can be explained in terms of the spins of electrons and holes involved in the different excitonic transitions:[48] in the emission process is always involved a hh state, i.e., mainly $J_z=\pm\frac{3}{2}$, and according to recent calculations the relaxation of holes occurs preferentially with conservation of hole parity,[47] i.e., a $J_z=-\frac{1}{2}$ ($+\frac{1}{2}$) lh state relaxes to a $J_z=+\frac{3}{2}$ ($-\frac{3}{2}$) hh state. Since the spin-relaxation time of the holes is much shorter than that of the electrons, $\sim$5 ps vs $\sim$150 ps,[27] this explains the intensity changes seen in Fig. 8(a). Let us consider σ^+ excitation: $l_1(1s)\uparrow$, mainly composed of a $J_z=+\frac{1}{2}$ hole and a $J_z=+\frac{1}{2}$ electron, will preferentially relax to a hh exciton formed by a $J_z=-\frac{3}{2}$ hole and the same $J_z=+\frac{1}{2}$ electron; this is the $h_1(1s)\downarrow$ observed in the σ^- emission. Therefore this state shows a negative degree of polarization ($\mathcal{P}=-33\%$).[49] On the other hand, in the case of $h_1(2s)\uparrow$ ($J_z=+\frac{3}{2}$ hole and $J_z=-\frac{1}{2}$ electron) the relaxation takes place mainly to its excitonic ground state with the same spin orientation, $h_1(1s)\uparrow$ observed in σ^+ emission, thus having a positive degree of polarization ($\mathcal{P}=+15\%$). The same arguments can also be applied to the excitons created with σ^- polarized light.

The conservation of the magnetic moment of the electrons involved in the higher excited states is only observed in samples of good quality and for magnetic fields high enough to reduce the overlap between the two orthogonally polarized emissions, as has been also observed by Potemski and co-workers.[25] In our [111]-oriented samples the width of the PL hinders the observation of this effect up to the highest field available in our experiments. However, an unusual result is obtained for the degree of polarization of $h_1(1s)$ as a function of the magnetic field. Figure 9 depicts the degree of polarization of $h_1(1s)$ in the 100-Å-wide QW for σ^+ (solid points) and σ^- excitation (open points) as a function of the magnetic field. The detection of the emission was always done at the peak of the PL, which lies $\sim$3 meV below the peak in the PLE. We are considering now the case of quasiresonant creation of excitons. In this situation, all the intermediate states of interest during the absorption, energy and spin relaxation, and emission processes are correlated electron-hole pairs.[50] However, one must consider that the initial and final states are not the same, since we are pumping free excitons, while the PL is due to excitons bound to some genre of defect in the QW. The values of the polarization at zero field ($\sim$40%) indicate that the spin scattering time is not very short on the scale of the total excitonic lifetime, and the decrease of the polarization with magnetic field denotes that the spin-flip rate of the free exciton during its energy relaxation to the bound exciton increases.

Although a strong sample dependence of the spin-relaxation rate, and therefore of the cw polarization, has been found in $GaAs/Ga_xAl_{1-x}As$ QW's,[51] our results present a systematic decrease of the degree of polarization with increasing magnetic field for the different samples. The zero-field degree of polarization is 45±10 % for all the samples, including the [001]-oriented QW, while the drop between 0 and 13.5 T varies from 10% (130-Å QW) to 40% (75-Å QW). In the case of the [001]-oriented QW, at high fields, when the oppositely polarized emissions are split, $\mathcal{P}$ depends markedly on the energy where the PL is detected, especially at energies where the overlap between the two polarizations diminishes. Nevertheless, a decrease of the polarization is also observed for this sample up to $\sim$9 T.

The process of spin relaxation of excitons in QW's has not been considered theoretically so far. The polarization

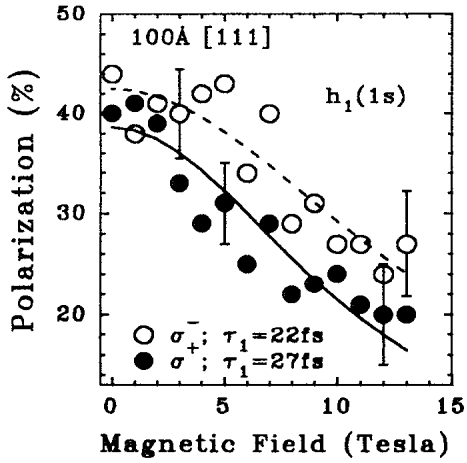

FIG. 9. Degree of polarization vs magnetic field for quasiresonant excitation of the heavy-hole exciton, $h_1(1s)$, in a 100-Å [111]-oriented QW. The lines represent the best fit with Eq. (3) (see text).

of the PL of QW's, neglecting the spin depolarization in the conduction band and assuming complete spin relaxation of the photoexcited holes, has been calculated by Twardowski and Hermann.[52] Their calculations explain qualitatively in terms of the valence-band structure previous results of the polarization spectrum in undoped QW's, which show that the hole polarization is not very important.[45] However, more recent calculations,[47] considering the hole relaxation processes by emission of acoustic phonons, show that the hole-spin relaxation is incomplete in QW's. Spin-flip scattering of holes in QW's has also been recently studied considering the interaction of holes with static scatterers.[53] This study shows that the spin-relaxation time can become much longer than the recombination time when the kinetic energy of the holes is small compared with the hh-lh separation. Actually, the spin-flip scattering times of holes becomes very large as $\mathbf{k}$ tends to zero,[53] however, in the case of excitons as they sample a finite region of $\mathbf{k}$ space, the spin-flip scattering time becomes finite. For electrons, the D'yakonov-Perel' (DP) mechanism[54] has been proposed as the relevant one to flip the electron spin in QW's at high temperatures.[45] In recent calculations of the spin-flip relaxation time of QW electrons in a magnetic field,[55] Bastard finds for the DP mechanism an increase of this time in the $n=0$ Landau level amounting to 1.6 when the magnetic field is increased from 6 to 15 T.

Studies of the time decay of the polarization in QW's have found that the spin relaxation of the excitons must be considered as a whole, since independent spin relaxation for electrons and holes cannot describe the experimental results.[27,56,57] Moreover, if the spin relaxation of the excitons could be considered as arising from the spin relaxation of the electrons and holes separately, one should expect an increase of the degree of polarization in the presence of a magnetic field, as a consequence of the increase in the spin-relaxation time of the electrons.[55,58] Furthermore, in two-dimensional systems, in the presence of a magnetic field, the level spectrum is discrete, thus a slowing down of any kind of interlevel relaxation of the carriers should be expected when compared to the zero-field situation.[55]

From the previous considerations, it is clear that a different mechanism should be responsible for the decrease of the degree of polarization with increasing magnetic field, when the field is applied in the Faraday configuration. By analogy with the effect of a longitudinal magnetic field on the circular polarization of the hot luminescence in GaAs,[59,60] we have fitted the degree of polarization as a function of magnetic field using a Lorentzian expression:

$$\mathbf{P}(H)=\frac{\mathbf{P}(0)}{1+\omega_c^{r2}\tau_1^2}\ , \tag{3}$$

where ω_c^r is the reduced cyclotron frequency and τ_1 represents an effective out-scattering time due to any processes of energy relaxation from the free exciton to the bound exciton. The decrease of circular polarization with magnetic field, in Faraday configuration, is interpreted in the case of hot luminescence as a manifestation of the correlation between momenta and spins of the photoexcited carriers.[60] In our case, we presume that the same mechanism is also valid for excitons.

In Eq. (3), ω_c^r was obtained from the reduced effective mass of the excitons. The results of the fits, using $\mathcal{P}(0)$ and τ_1 as adjustable parameters, are shown in Fig. 9 as a solid (dashed) line for σ^+ (σ^-) excitation. The values of τ_1 in [111]-oriented QW's range from 10($\pm$10) fs in σ^+ polarization for the 75-Å sample up to 27($\pm$10) fs for the 100-Å sample. The uncertainties in τ_1 are rather large since ω_c^r is also obtained through a fitting procedure. The fact that the out-scattering times do not show any systematic dependence on QW width is not surprising since the defects to which the excitons bound may randomly fluctuate from sample to sample. In the case of the [001] QW, a fitting up to 9 T of the degree of polarization yields a value of τ_1 of 28($\pm$10) fs, of the same magnitude as those obtained in [111] QW's, thus indicating that the process of relaxation from free to bound excitons does not depend strongly on crystallographic orientation.

VI. SUMMARY

We have studied the magnetooptical properties of [111]-oriented GaAs/$Ga_xAl_{1-x}As$ QW's by means of circularly polarized PLE spectroscopy. An analysis of the fan diagrams of the magnetoexcitons, using an hydrogenic model, yields accurate values for the binding energies and reduced effective masses of the excitons. We find a decrease of the hh exciton reduced effective masses in [111] QW's as compared with those values for [001]-oriented QW's, while the lh band is isotropic, in agreement with $\mathbf{k}\cdot\mathbf{p}$ theory. The study of the polarization of the emitted light and its magnetic-field dependence indicates that a reduction of the degree of polarization takes place in Faraday configuration. This fact is interpreted, by similarity with the effect observed in hot luminescence in GaAs, as a decrease of the correlation between momenta and spins of the excitons as they decay from free to bound excitons. However, we believe that the process of spin relaxation of excitons in QW's is not well understood and further experimental data are required.

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