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Spin relaxation in intrinsic GaAs quantum wells: Influence of excitonic localization

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We have investigated exciton spin relaxation in GaAs quantum wells by picosecond time-resolved photoluminescence spectroscopy, in order to determine the origin of spin-relaxation processes and their dependence on excitonic localization. The studies have been done as a function of excitation and detection energy, lattice temperature, and carrier density. The excitation-energy dependence of the polarization decay time indicates that exchange interaction is the leading spin-relaxation mechanism at low temperature. However, we have not been able to explain the high-temperature ($T \geq 50$ K) dependence of the polarization decay time with either the D'yakonov-Perel' mechanism or with the exchange interaction. We have also found that spin relaxation is strongly affected by excitonic localization.

I. INTRODUCTION

Spin relaxation of excitons and free carriers in bulk semiconductors has been extensively investigated in the past,[1-3] and different basic mechanisms have been identified. In semiconductor quantum wells (QW's) the relative importance of these mechanisms is modified basically for three reasons:[4] (i) electronic band structure, which strongly affects the hole spin relaxation, (ii) enhancement of the excitonic interaction, leading to a strong spin relaxation due to exciton exchange, and (iii) higher carrier mobility, which is important to mechanisms sensitive to carrier momentum relaxation, such as the D'yakonov-Perel' mechanism. Therefore, new spin-dynamics properties are expected.

Spin relaxation of free carriers has been studied in doped QW's and a decrease (increase) of the spin-flip time of electrons (holes) as compared with the bulk values has been found.[5,6] The observed enhancement of the hole spin-relaxation time is in agreement with the predictions of some theoretical works which had anticipated an increase as a consequence of the lift of the fourfold degeneracy at the top of the valence band.[7,8] However, despite this qualitative accord, there is a large dispersion in the experimental data, ranging from 4 ps (Ref. 5) to 1 ns (Ref. 6), and quantitative comparisons of experimental and theoretical results are scarce.[7]

Exciton spin relaxation has been investigated in intrinsic QW's,[5,9-16] and two different processes have been considered. Some authors have found indications of exchange interaction being the leading spin-relaxation mechanism at low temperatures, which would imply a simultaneous spin flip of electrons and holes.[5,9,16] However, others have discussed their results considering exciton spin relaxation as a consequence of the consecutive spin flip of the electron and the hole forming the exciton.[13] In a recent paper, a theory of exciton spin relaxation driven by the exchange interaction has been given by Maialle, de Andrade e Silva, and Sham.[17] That work revealed the importance of including in the analysis of the data both the single-particle (electron and hole) spin-flip processes and the excitonic process. Taking this into account, Vinattieri *et al.* have concluded, from resonant measurements done at low temperatures in the presence of an external electric field, that exciton spin relaxation is dominated by exchange interaction.[16]

In spite of these efforts, it is the general opinion that further experimental and theoretical works are needed to reach a full comprehension of spin relaxation in semiconductor QW's,[4] and that localization effects could play an important role in spin relaxation, being the origin of the large dispersion in the data obtained up to now. Exciton localization is usually manifested in QW's by the presence of a shift between the heavy-hole excitonic peaks of the photoluminescence and photoluminescence excitation spectra, the so called "Stokes shift." Bastard *et al.* explained the Stokes shift in terms of exciton trapping at random interface defects,[18] and obtained the result that Stokes shifts smaller than ~10 meV could be due to intrinsic interface defects with lateral size of the order of 200 Å. Nowadays, it is generally accepted that good samples can exhibit Stokes shifts of a few meV, and that they are due to the difference in the binding energy between free and bound excitons.

Our purposes in this work are the study of the origin of spin-relaxation processes, and the examination of their dependence on excitonic localization. In this paper we report results obtained in a GaAs QW which, although displaying at 2 K and very low carrier densities a Stokes shift of ~2.5 meV, exhibits excitonic dynamic properties analogous to those observed in very high-quality samples with vanishing Stokes shifts.[19] The investigations have been done by varying the excitation and detection energy, the carrier density, and the lattice temperature. Our results show indications of exchange interaction being the leading spin-relaxation mechanism at low temperatures.

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We have also found that localization, even though not strong enough to change the exciton dynamics, markedly modifies spin-relaxation processes. The Stokes shift has allowed us to study the dynamics of resonantly created heavy-hole excitons. In that case, we have found, in agreement with recent works,[15,16] a fast initial decay of the photoluminescence which is due to the removal of excitons from optically active states to dark states. Our studies have revealed a strong dependence of this process on excitonic localization.

This manuscript is organized as follows. Section II introduces the theory of the different spin-relaxation mechanisms. The experimental details are given in Sec. III. The dynamical properties of our sample are reported in Sec. IV A. The results related to the filling of the dark excitonic states and its dependence on excitonic localization are given in Sec. IV B. Section IV C compiles the observed dependence of spin-relaxation processes on excitation and detection energy, carrier density, and lattice temperature. Finally, we summarize in Sec. V.

II. SPIN-RELAXATION MECHANISMS

The spin state of an exciton is a direct produce of the conduction-electron and valence-hole spin states. In a III-V direct-gap semiconductor the z component of the total angular momentum (which in the following will be named the "spin") of electrons in the conduction-band edge has values $\pm\frac{1}{2}$, while the possible values for electrons in the heavy-hole (light-hole) valence-band edge are $\pm\frac{3}{2}(\pm\frac{1}{2})$. For heavy-hole excitons the total exciton spin can be ± 1 or ± 2. The former are optically active while the latter cannot be photoexcited. Exciton spin can be relaxed via the spin relaxation of either constituent, electron or hole, or via simultaneous spin flip of both constituents.[4] Several mechanisms are usually invoked to account for the spin relaxation of electrons, holes, and excitons.

A. Electron spin relaxation

Two mechanisms are commonly considered for electron spin relaxation in intrinsic semiconductors. In the Elliot-Yafet mechanism,[20] the mixing, through the $\mathbf{k}\cdot\mathbf{p}$ term, between conduction-band and valence-band states induces the spin relaxation. Valence-band states, which are connected to conduction-band states of opposite spins, may be coupled by acoustic phonon or impurity scattering, therefore leading to conduction-band electron spin relaxation. As a consequence of the band-gap energy in the denominator of the $\mathbf{k}\cdot\mathbf{p}$ term, this process is usually considered as weak in wide-gap bulk semiconductors, such as GaAs. However, its importance should be reexamined in quantum wells.[4] The D'yakonov-Perel' (DP) mechanism contemplates the spin-flip processes as a result of the asymmetry of the constituent atoms in the III-V compound with the zinc-blende structure.[21] The anisotropic, cubic in $\mathbf{k}$ term of the conduction-band dispersion relation couples conduction-electron states of opposite spins. This term may be represented as an internal effective magnetic field which is wave-vector dependent. Therefore, as the electron momentum is changed by any scattering event, the magnetic field fluctuates, causing spin relaxation.

D'yakonov and Kachorovskii have shown that, in the case of quantum wells, for nondegenerate carriers, the spin-relaxation rate of electrons in the first confined state, due to the anisotropy of the conduction-band dispersion relation, is[22]

$$\frac{1}{\tau_e^{\mathrm{DP}}}=\frac{2\alpha E_1^2 k_B T}{E_g \hbar^2}\tau^* , \tag{1}$$

where α is a numerical coefficient governing the spin splitting of the conduction band (in the case of GaAs $\alpha=0.07$), E_1 is the first confined state in the QW, and E_g the band gap. τ^* is the electron momentum relaxation time, which, to obtain Eq. (1), has been supposed to be energy independent.[23]

B. Hole spin relaxation

The strength of mixing in the valence band plays a fundamental role in hole spin relaxation. For III-V semiconductors, the heavy-hole and light-hole mixing can be included by expanding the valence-band wave functions about the Bloch states at the Γ_8 valence-band maximum.[7,8] If the growth axis is taken as the z direction, valence-band wave functions for subband ν may be written as[7,8]

$$\psi_{\nu\mathbf{k}_\perp}(\mathbf{r})=e^{i(k_x x+k_y y)}\sum_m \zeta_m(\nu\mathbf{k}_\perp,z)\mathbf{u}_m , \tag{2}$$

where the index $m=\frac{3}{2},-\frac{1}{2},\frac{1}{2},-\frac{3}{2}$, $\mathbf{k}_\perp$ is the in-plane wave vector, and the $\zeta_m(\nu\mathbf{k}_\perp,z)$ are the envelope functions. Since for $\mathbf{k}_\perp\neq 0$ all the $\zeta_m(\nu\mathbf{k}_\perp,z)$ are not zero, the spin components are mixed, and spin is not a good quantum number. Therefore, it is convenient, for a symmetric quantum well, to classify valence-band states by a parity number $p=\pm 1$ under the mirror reflection $z\rightarrow -z$.[7] In a state with parity p, ψ_p, the envelope function with index $m,\zeta_m(\nu\mathbf{k}_\perp,z)$, has parity p_m given by[7]

$$p_m=p(-1)^{3/2-m} . \tag{3}$$

For heavy-hole valence-band states with $\mathbf{k}_\perp=\mathbf{0}$, the only nonvanishing $\zeta_m(\nu\mathbf{k}_\perp,z)$ are those with $m=\pm\frac{3}{2}$, and the spin of ψ_{+1} (ψ_{-1}) is $+\frac{3}{2}(-\frac{3}{2})$. In this case, the band mixing vanishes, and the spin-flip time is expected to diverge.[8] For $\mathbf{k}_\perp\neq\mathbf{0}$, hole spin relaxation occurs when the envelope functions are changed as a consequence of scattering processes,[7,8] and a strong dependence of the spin-flip time on band mixing has been anticipated.[8]

C. Exciton spin relaxation

The two previous mechanisms can modify the spin state of an exciton by changing the individual spin of the electrons and/or the holes. If only one of these processes occurs, an optically active exciton would go from a spin ± 1 state to a spin ± 2, dark state. For the sake of clarity, let us consider a resonantly created heavy-hole $|+1\rangle$ exciton, which was excited with σ^+ polarized light; the individual spins of the electron and hole are $-\frac{1}{2}$ and $+\frac{3}{2}$, respectively.[24] If the electron (hole) changes its spin to $+\frac{1}{2}(-\frac{3}{2})$, the resulting exciton spin would be $+2(-2)$; thus an optically inactive state ensues. A consecutive spin-flip process of the hole (electron) would bring the exciton to the optically active $|-1\rangle$ state.

Furthermore, the spin relaxation of excitons between the optically active $|+1\rangle$ and $|-1\rangle$ states may occur in a single-step process driven by the exchange interaction. The theory of this mechanism in quantum wells has been given recently by Maialle, de Andrade e Silva, and Sham.[17] The exchange term in the effective-mass equation for quantum-well excitons may be separated into a long-range and a short-range part. Considering only heavy-hole excitons, the coupling between the $|+1\rangle$ and $|-1\rangle$ states due to the long-range exchange interaction is of the form[4,17]

$$H_{\text{hhe}}^{\text{LR}} \propto \frac{|\Phi_{1s(\text{hh})}(0)|^2}{K} \Delta E_{\text{LT}} K_\alpha K_\beta f(k) , \tag{4}$$

where $\Phi_{1s(\text{hh})}(0)$ is the heavy-hole exciton wave function at zero relative distance, K_α is a component of the total momentum of the exciton, ΔE_{LT} is the longitudinal-transverse splitting in the bulk semiconductor, and $f(k)$ is a form factor that contains the overlap integral between electron and hole wave functions in the growth axis direction. From Eq. (4), it is clear that spin-flip processes will be more important for large-**K** excitons and for tighter-bound excitons. The short-range exchange interaction, which is of the form $\boldsymbol{\sigma}_e \cdot \mathbf{J}_h$, where $\boldsymbol{\sigma}_e$ and $\mathbf{J}_h$ are the electron and hole spin vectors, conserves total spin, and, therefore, forbids the direct transition between the optically active heavy-hole exciton spin states $(-\frac{1}{2},+\frac{3}{2})$ and $(+\frac{1}{2},-\frac{3}{2})$.[17] In this case, to obtain a spin-flip process it is necessary to consider an additional spin-nonconserving mechanism, such as, for example, valence-band mixing. Therefore the short-range exchange contribution to the exciton spin relaxation is considerably weaker than that from the long-range term.[17]

As in the DP mechanism, the coupling between $|+1\rangle$ and $|-1\rangle$ states due to the exchange interaction may be considered as the result of a **K**-dependent effective magnetic field. Spin relaxation occurs when, as the exciton scatters, the direction of this field changes. Thus the exciton spin-relaxation rate is proportional to the exciton momentum relaxation time.[17]

III. EXPERIMENTAL DETAILS

We report on exciton spin relaxation in a GaAs/AlAs multiple quantum well, consisting of 50 periods of nominally 77-Å-wide GaAs wells and 72-Å-wide AlAs barriers. The sample was exceptionally bright as compared with similar QW's investigated in our laboratory, and presented a small Stokes shift of ~2.5 meV. The experiments were performed in a temperature-variable, cold-finger cryostat exciting with pulses from a Styryl 8 dye laser, tunable from 810 to 720 nm. The incident light was directed along the growth axis and a backscattering geometry was used. The dye laser was synchronously pumped by the 532-nm line of a mode-locked Nd:YAG laser (where YAG is yttrium aluminum garnet). The photoluminescence (PL) was time resolved in a standard upconversion spectrometer. The time resolution, obtained by overlapping on a nonlinear crystal, LiIO_3, the luminescence from the sample with a delayed pulse from the laser, is basically determined by the width of the pulse, which in our case is 6 ps. A double-grating monochromator was used to disperse the upconverted signal. The exciting light was circularly polarized by means of a $\lambda/4$ plate, and the PL was analyzed into its σ^+ and σ^- components using a second $\lambda/4$ plate before the nonlinear crystal.

IV. RESULTS AND DISCUSSION

In Fig. 1 we show the cw PL (thick line) and the photoluminescence excitation (PLE) spectra (thin line) of our sample. The spectra were recorded at 2 K under very low excitation density (5 mW cm^{-2}). In the PLE spectrum, the peaks corresponding to the heavy-hole (hh) and light-hole (lh) excitons are clearly seen at 1.617 and 1.645 eV, respectively. The onset of the hh subband continuum is also observed at 1.626 eV. The Stokes shift between the hh exciton peaks in PL and PLE spectra, amounting to ~2.5 meV, is too small to be attributed to a monolayer fluctuation. With increasing temperature the Stokes shift decreases, and it vanishes at 40 K. Therefore we believe that at low excitation densities and temperatures the PL arises from excitons bound to some kind of defects, either impurities or interface defects. The time-resolved experiments are done under pulsed excitation and the carrier densities are much larger than those used in cw conditions. Under high excitation a saturation of the bound-exciton contribution to the PL is expected and the importance of the free-exciton emission will be enhanced. This fact is borne out by our cw experiments, since the Stokes shift decreases by 1 meV when the excitation density is increased by four orders of magnitude. The inset in Fig. 1 displays the temperature dependence

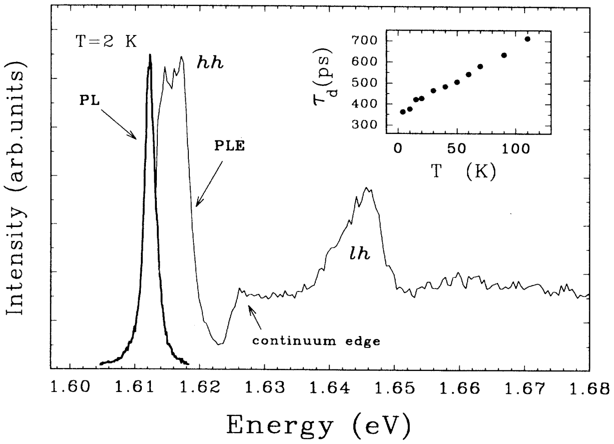

FIG. 1. Photoluminescence (thick line) and photoluminescence excitation spectra (thin line) recorded at 2 K under an excitation density of 5 mW cm^{-2}. The inset shows the temperature dependence of the decay time of the photoluminescence for an initial carrier density of 4×10^{10} cm^{-2}.

of the PL decay time measured at the peak of the time-resolved luminescence band for an initial carrier density ρ of 4×10^{10} cm^{-2}. The monotonic linear increase with increasing temperature, which is characteristic of free excitons,[25] corroborates that the contribution of free excitons to the emission grows at high excitation densities.

A. Exciton dynamics

Due to the strong dependence that spin-flip mechanisms have on the carrier energy and wave vector (see Sec. II), spin relaxation cannot be studied without considering carrier dynamics. Thus we report in this section the exciton dynamics properties of our sample. Figure 2 shows the time evolution of the sum of the σ^+ and σ^- components of the luminescence excited with σ^+ polarized light at two different energies, 1.617 eV (curve *a*, filled circles) and 1.630 eV (curve *b*, open circles). Both sets of time profiles were recorded at 4 K with the same exciting power, corresponding to an initial carrier density of 4×10^{10} cm^{-2}, and the detection energy was set at the maximum of the PL band. The time profiles are in agreement with the current understanding of exciton formation and relaxation,[19] which, basically, separates the relaxation process that follows the optical creation of an electron-hole pair of the continuum into two steps. First, in a time of the order of tens of picoseconds, the electron-hole pair relaxes its energy and forms an exciton with large kinetic energy. In the second step, the excess energy is lost in a slow process (that lasts hundreds of picoseconds) which brings the exciton to states with center-of-mass momentum (**K**) near to zero, where it may recombine, emitting a photon. The large difference in the rise times of the two curves in Fig. 2 reflects the fact that curve *b* corresponds to the excitation of electron-hole pairs in the subband continuum, and excess energy has to be lost before the exciton can recombine.

On the other hand, in the case of curve *a*, the 1*s*-hh excitons have been created resonantly with $\mathbf{K}=0$, and they can directly couple to light. The fast initial decay observed in trace *a* is related to the filling of dark excitonic states due to hole spin flip, and it will be discussed in the next section.

Further insights into exciton momentum relaxation processes are obtained from the temperature and carrier-density dependence of the time evolution of the photoluminescence. Figure 3(a) shows time profiles of the PL, for a carrier density of 4×10^{10} cm^{-2}, at different temperatures. The detection energy was set at the maximum of the PL and a difference of 20 meV between excitation and detection was kept for all the temperatures. The data have been fitted to a two-level dynamical model which includes two characteristic times, the formation time of excitons with $\mathbf{K}=0$, τ_f, and the exciton radiative recombination time. The solid lines in the figure depict the results of the fits. The temperature dependence of τ_f is shown in the inset of Fig. 3(a). The decrease of τ_f with increasing temperature is a consequence of the spreading of the thermalized exciton distribution around $\mathbf{K}=0$ as temperature increases.[19] Therefore the initial distribution of large-**K** excitons approaches the final $\mathbf{K}=0$ distribution faster at high temperatures.

The time profiles of the PL, normalized to the maximum intensity, for different carrier densities at 4 K are

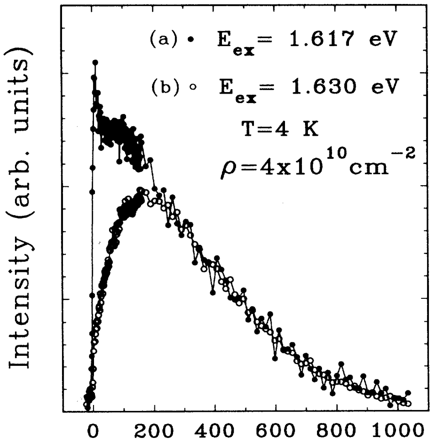

FIG. 2. Time evolution of the sum of the σ^+ and σ^- components of the luminescence. Curve *a*: Excitation at 1.617 eV (filled circles). Curve *b*: Excitation at 1.630 eV (open circles). The lattice temperature and the initial carrier density are 4 K and 4×10^{10} cm^{-2}, respectively.

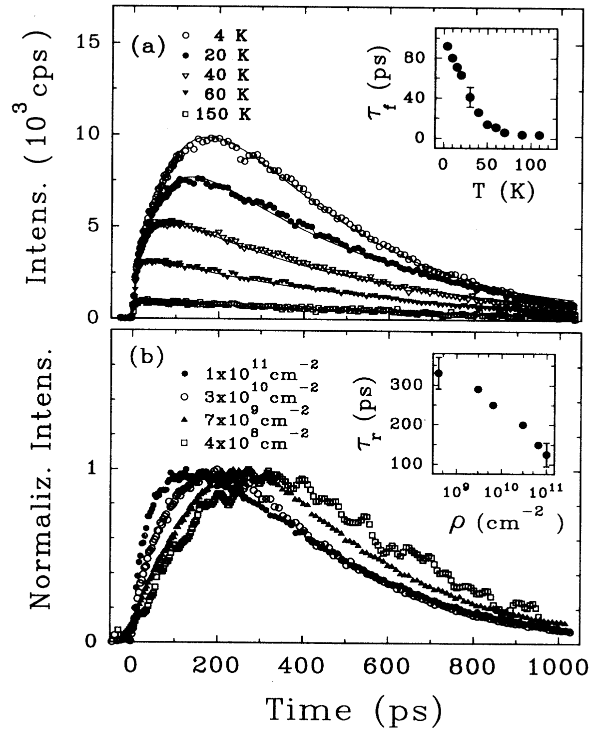

FIG. 3. (a) Time evolution of the sum of the σ^+ and σ^- components of the luminescence excited with a carrier density of 4×10^{10} cm^{-2} for different temperatures. The solid lines depict the fits to a dynamical model (see text). The inset shows the *T* dependence of the formation time. (b) Normalized time evolution of the PL at 4 K for different carrier densities. The inset depicts the carrier-density dependence of the rise time.

depicted in Fig. 3(b). Since for carrier densities of $\sim 7\times10^{9}$ cm^{-2} and lower the two-level model does not properly fit the experimental data, it has not been applied to these results. Therefore the rise time of the PL, τ_r, defined as the time needed to reach the maximum intensity, is used to characterize the exciton formation. The decrease in the rise time, as the carrier density is increased, agrees with the idea that exciton-exciton collisions are important in the relaxation processes of large-**K** excitons to $\mathbf{K}=0$ excitons.[19]

B. Filling of dark excitonic states

The initial behavior of the photoluminescence may bring out information about the removal of excitons from optically active states to dark states. We have found that this behavior depends strongly on excitation and detection energies. Let us consider, first, the resonant excitation of excitons with $\mathbf{K}=0$. Figure 4 compiles the time evolution of the σ^+ (circles) and σ^- (squares) photoluminescence for two different detection energies, 1.612 eV (black symbols) and 1.611 eV (gray symbols), and a lattice temperature of 4 K. The excitation was done at 1.617 eV with an initial carrier density of 4×10^{10} cm^{-2}. The inset shows the PL spectra excited at 1.619 eV, for a delay of 300 ps. The two arrows mark the detection energies used to measure the time evolution.[26] Two difference between black and gray traces can be distinguished in the figure. One is the fast initial decay in the black σ^+ trace, which is absent in the gray one. The other is the time in which circles and squares of the same color merge, which is shorter for the gray symbols. This feature, which determines the polarization decay time, will be discussed in Sec. IV C 3. Now, we will concentrate on the initial behavior of the σ^+ photoluminescence. We have carefully checked that the fast decay observed detecting at 1.612 eV is not a spurious signal from the laser pulse: the autocorrelation trace of the pulse is much narrower than the observed initial behavior. Furthermore, detecting at 1.611 eV and exciting with the same excess energy employed to record black traces, 5 meV, the fast initial decay was also absent.

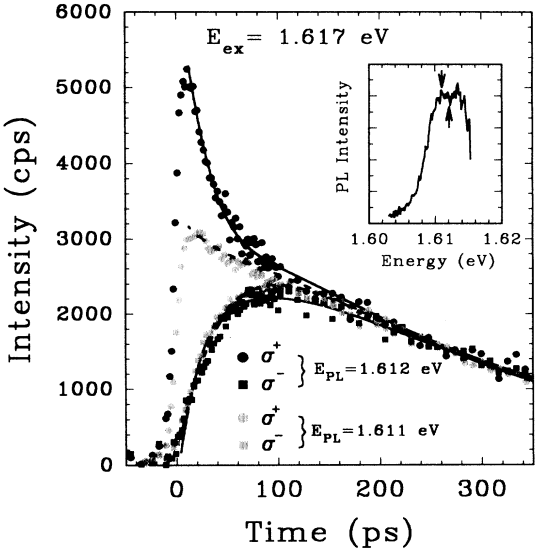

FIG. 4. Time evolution of the σ^+ (circles) and σ^- (squares) photoluminescence detected at 1.612 eV (black symbols) and at 1.611 eV (gray symbols). The excitation was done at 1.617 eV with σ^+ light and an initial carrier density of 4×10^{10} cm^{-2}. The lattice temperature was 4 K. The solid lines (dashed lines) show the fit of the black (gray) curves to a dynamical model such as the one used in Ref. 15. The inset shows the PL spectra, for a delay of 300 ps.

It has been predicted that removal of excitons from optically active states to dark states, via the spin flip of a single particle of the exciton, would give rise to a fast initial decay of the luminescence.[17] This behavior has been observed in GaAS QW's under resonant excitation by Vinattieri *et al.*[15,16] Fitting their data with a model which takes into account spin flip of the exciton, as well as spin flip of electrons and holes individually, they have ascribed the initial decay to the spin flip of the holes. We are also able to fit our data using the same model. The time profiles corresponding to a detection energy of 1.612 eV in Fig. 4 are well fitted (solid lines) using a spin-flip time for the holes (electrons) of $\tau_h=25\pm8$ ps ($\tau_e=200\pm100$ ps) and an exciton spin-flip time of $\tau_x=35\pm10$ ps. Therefore we believe that the removal of excitons from $|+1\rangle$ states to dark $|-2\rangle$ states as the holes relax their spins is the mechanism responsible for the initial time behavior of the σ^+ luminescence. We should also mention that analogous time profiles are obtained for σ^- exciting and detecting polarizations, but in this case the active and dark excitonic states are $|-1\rangle$ and $|+2\rangle$, respectively. The relatively long spin-flip time for the holes, as compared with that measured in *n*-doped samples of ~ 5 ps,[5] is a consequence of the excitonic nature of the PL. Holes correlated to electrons, forming excitons, have larger spin-relaxation times than uncorrelated ones due to the smaller phase space available for scattering.[4]

We believe that the difference between black and gray σ^+ traces in Fig. 4 is due to the influence of excitonic localization on the spin-flip time of holes correlated to electrons. Bastard *et al.*[18] using a semi-Gaussian interface-defect model, have calculated that, for localized excitons on defects with the same depth, a change in lateral size of ~ 100 Å produces a variation of ~ 1 meV in their binding energy. Changing the detection energy from 1.612 to 1.611 eV in Fig. 4, we are sampling excitons with larger binding energies, and thus with stronger localization. The uncertainty in the in-plane center-of-mass momentum, $\Delta\mathbf{K}_\perp$ of these tighter-bound excitons will be larger. As $\mathbf{K}_\perp=\mathbf{k}_{e\perp}+\mathbf{k}_{h\perp}$, where $\mathbf{k}_{e\perp}$ and $\mathbf{k}_{h\perp}$ are electron and hole in-plane wave vectors, the uncertainty in momentum of correlated electrons ($\Delta\mathbf{k}_{e\perp}$) and holes ($\Delta\mathbf{k}_{h\perp}$) depends on the degree of excitonic localization. Hole spin relaxation, which is due to valence-band mixing, shows a strong dependence on $\mathbf{k}_{h\perp}$; the relaxation rate increases with increasing wave vector.[8] Therefore, keeping in mind that only $\mathbf{K}_\perp\approx 0$ excitons can couple to light, for stronger localized excitons, which have a larger $\Delta\mathbf{k}_{h\perp}$, a shorter spin-flip time of the holes is expected. As a matter of fact, the time profiles detected at 1.611 eV in Fig. 4 are fitted with $\tau_h = 5 \pm 5$ ps and $\tau_x = 20 \pm 10$ ps (dashed line in Fig. 4), keeping the rest of the times the same as those used when detecting at 1.612 eV. Since τ_h is of the order of our time resolution, the initial fast decay is not observed in this case.

The initial fast decay is also observed by exciting at the onset of the subband continuum. Figure 5 shows two different time evolutions of σ^+ polarized PL excited at the continuum onset (1.626 eV, trace *a*) and above the subband edge (1.630 eV, trace *b*). At the excitation energy of case *a*, we are creating uncorrelated electron-hole pairs, as well as higher excited states ($ns; n \geq 2$) of the hh exciton. The initial decay could arise from the spin relaxation of the holes which belong to these excited excitonic states. The additional slow rise of the PL is due to the cooling of the large-**K** excitons. In the case of creating only uncorrelated electron-hole pairs (Fig. 5, trace *b*), the spin-relaxation time of the holes is much shorter than in the correlated case,[5] and therefore no indication of their spin relaxation is observed. The initial fast rise of the PL observed in both curves seems to indicate that some excitons reach the $\mathbf{K}=0$ state by a very fast process which is of the order of our time resolution. Further investigations of this behavior are in progress and will be reported in a future paper.

C. Spin relaxation

To obtain spin-relaxation times from the experimental data it is necessary to fit the time evolutions of the σ^+ and σ^- PL with an appropriate dynamical model, such as the one used for the data in Fig. 4. The results shown up to now reveal the great complexity of spin relaxation, which implies the use of dynamical models with a large number of parameters. In order to avoid the drawbacks inherent in too-parameterized models, we have chosen to use the degree of circular polarization $\mathcal{P}$, whose time evolution can be fitted to a single exponential decay, to obtain a phenomenological insight into those mechanisms.

The degree of circular polarization is defined, for one of the exciting helicities, as the fractional difference of the PL intensities of the two circular polarizations, σ^+ and σ^-, at a given energy: i.e., for σ^+ excitation, $\mathcal{P}=(I^+ - I^-)/(I^+ + I^-)$. The decay time of $\mathcal{P}$, $\tau_{\mathcal{P}}$, represents an "effective spin-relaxation time."

1. Excitation-energy dependence

We present in Fig. 6 (solid points) the dependence of the polarization decay time on excitation energy, detecting at the peak of the PL at 4 K for an initial carrier density of 4×10^{10} cm^{-2}. The line depicts the cw PLE spectrum. The decrease of $\tau_{\mathcal{P}}$, moving away from resonance, can be linked to an increase of the long-range exchange interaction. It has been proposed that the high-energy tail in the pseudoabsorption arises from a partial violation of the **K**-conserving rule, which allows the creation of large-**K** excitons.[27] According to Eq. (4), the coupling between large-**K** $|+1\rangle$ and $|-1\rangle$ excitons will be larger, leading to an increase in the excitonic spin-flip rate. The same argument also applies for excitation above the subband continuum since large-**K** excitons are created from uncorrelated electron-hole pairs.

Information about the symmetry of the wave functions is also obtained from the excitation-energy dependence of the degree of polarization. In Fig. 7 we show the initial value of the polarization $\mathcal{P}(t_0)$ as a function of excitation energy $E_{\rm ex}$ for two different carrier densities when exciting with σ^+ light. $\mathcal{P}(t_0)$ is defined as the value of the polarization at time $t_0=3$ ps (half the width of the laser pulse). When exciting below the lh exciton, $\mathcal{P}(t_0)$ presents a marked dependence on $E_{\rm ex}$, increasing as the excitation energy decreases. For $E_{\rm ex}$ corresponding to the lh exciton, $\mathcal{P}(t_0)$ becomes negative and reaches values of about -20%. This negative value of the polarization is due to excitonic effects, which enhance the creation of

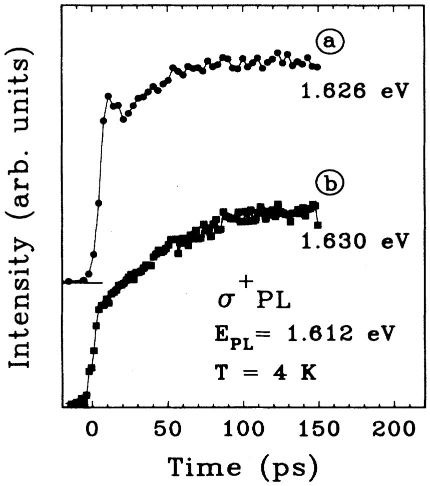

FIG. 5. Time evolution of the σ^+ PL excited with σ^+ light at 1.626 eV (circles) and at 1.630 eV (squares). The detection was set at the maximum of the PL (1.612 eV) and the initial carrier density was 4×10^{10} cm^{-2}.

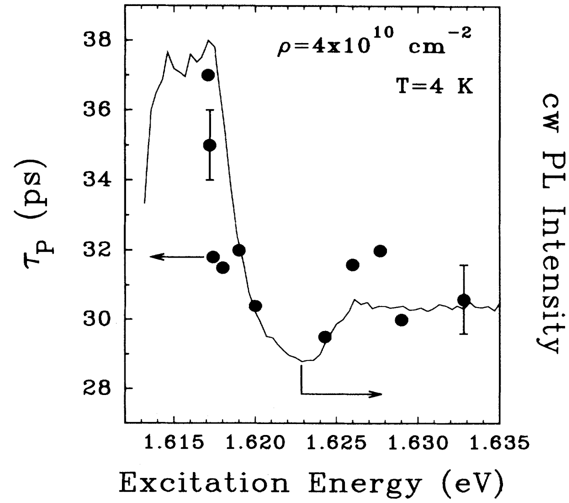

FIG. 6. Dependence of the polarization decay time (filled circles) as a function of excitation energy. The initial carrier density was 4×10^{10} cm^{-2}. The solid line shows the PLE spectrum.

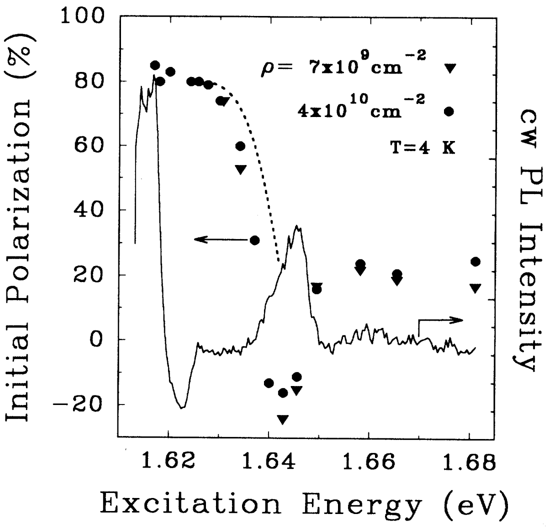

FIG. 7. Dependence of the initial value of the polarization on excitation energy for a carrier density of 7×10^{9} cm^{-2} (triangles) and of 4×10^{10} cm^{-2} (circles). The dashed line shows the result of a calculation based on valence-band mixing (see text). The solid line depicts the PLE spectrum.

light holes and electrons with spin $+\frac{1}{2}$. To observe the luminescence at the heavy-hole exciton, holes have to relax to $\pm\frac{3}{2}$ spin states. Since the spin-flip time of the electrons is considerably larger than t_0, a significant σ^- emission involving $+\frac{1}{2}$ and $-\frac{3}{2}$ holes is obtained. $\mathcal{P}(t_0)$ at the lh energy is considerably smaller than that at the hh exciton because holes belonging to the heavy-hole subband are also photocreated and they produce σ^+ emission. A similar dependence of $\mathcal{P}(t_0)$ on E_{ex} has been reported previously in the literature.[13,28]

For excess energy below the lh exciton, two different mechanisms could be responsible for the pronounced dependence of $\mathcal{P}(t_0)$ on excitation energy. The first one would be the increase of spin-relaxation rates of both electrons and holes with increasing energy. This is expected as a consequence of the energy dependence of τ_e^{DP} [see Eq. (1) and Ref. 22] for electrons, and of the valence-band mixing for holes. However, Damen and co-workers have shown that the spin-relaxation rate of holes is of the order of t_0^{-1} and more than one order of magnitude longer than that of electrons, and that the spin-flip rate of electrons does not depend strongly on excess energy.[5] Therefore, at t_0, only the spin flip of the holes will significantly change the spin of the $|+1\rangle$ initial state. The main effect of increased band mixing will be an enhancement in the rate of removal of $|+1\rangle$ excitons to $|-2\rangle$ dark excitons, without creation of $|-1\rangle$ states which are needed to explain the decrease in the degree of polarization. Thus this mechanism can be dismissed.

The second mechanism arises from the band mixing in the valence band, which for σ^+ excitation causes not only electrons from hh valence-band ψ_{-1} states to be promoted to $|-\frac{1}{2}\rangle$ conduction-band states, but also absorption between ψ_{+1} states and $|+\frac{1}{2}\rangle$ conduction electrons. We have calculated the populations of $|+\frac{1}{2}\rangle$ and $|-\frac{1}{2}\rangle$ conduction-band electrons in the envelope function approximation, taking valence-band mixing into account. The envelope functions were obtained by diagonalizing the off-diagonal terms of the Luttinger Hamiltonian in the basis spanned by the three lowest states at $\mathbf{k}_\perp=\mathbf{0}$: hh$_1$, lh$_1$, and hh$_2$.[29]

The strength of band mixing depends mainly on the energy difference between the hh$_1$ and the lh$_1$ subband, which is not the same as the splitting between hh$_1$ and lh$_1$ excitons. Therefore we have performed magneto-optical studies to obtain a precise value of this subband separation. A fitting of the fan diagrams, using the hydrogenic-like excitonic model described in Ref. 30, allowed us to determine the values of the hh$_1$ and lh$_1$ energies, which were used as an input for the band-mixing calculations.

To obtain $\mathcal{P}(t_0)$, we have assumed, for simplicity, a complete hole spin relaxation and neglected the electron spin relaxation. At the subband edge, where band mixing is negligible, the maximum value of $\mathcal{P}(t_0)$ is only 80%. This value would be obtained if $\sim 10\%$ of the excitons had flipped their spin from $|+1\rangle$ to $|-1\rangle$ at $t=t_0$. As a matter of fact, a spin relaxation time of ~ 30 ps, which is comparable with the measured polarization decay time (see Fig. 6), justifies the 20% drop in 3 ps. Therefore we have assumed that at all energies $\sim 10\%$ of the excitons have already flipped their spins at t_0.

The calculated degree of polarization, taken as the fractional difference between $|+1\rangle$ and $|-1\rangle$ populations, is plotted as a dashed line in Fig. 7. The reasonably good agreement between the measured and the calculated energy dependence of $\mathcal{P}(t_0)$ supports valence-band mixing as the origin of the drop of the polarization with increasing excess energy.

2. Carrier-density dependence

The time evolution of the polarization is shown in Fig. 8 on a semilogarithmic scale for three different initial carrier densities. The measurements were performed at 4 K, exciting at 1.630 eV, and detecting at the maximum of the PL. The lines represent the best fit to a monoexponential decay, from which the "effective" spin-flip times, $\tau_{\mathcal{P}}$, are obtained. A decrease of $\tau_{\mathcal{P}}$ with increasing carrier density is clearly seen.

The spin-relaxation times due to the DP mechanism and the exchange interaction are inversely proportional to the carrier momentum relaxation time.[4,17,22,23] Thus the carrier density may affect the value of $\tau_{\mathcal{P}}$ through the influence that screening may have on scattering processes. Although it is not possible to assess the relative importance of the different carrier scattering processes, it is known that, at low temperatures, mobility may be limited by scattering with residual ionized impurities.[31] Assuming this process as the main scattering mechanism, a rise in the carrier concentration will screen the Coulombic interaction with the charged impurities.[29] Therefore a decrease in the polarization decay time is expected, in agreement with the results of Fig. 8. It is, however, not possible from these data to determine the relative importance of the DP and exchange mechanisms.

A decrease of the polarization decay time with increas-

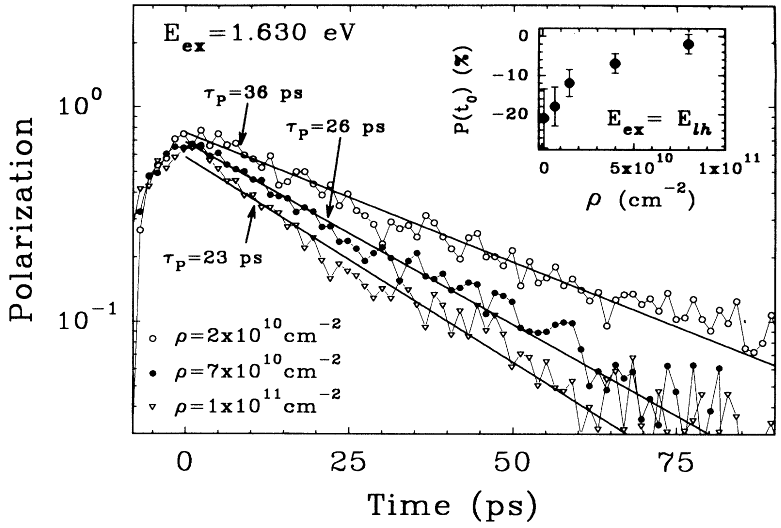

FIG. 8. Time evolution of the polarization for three different initial carrier densities (ρ). The measurements were performed at 4 K, exciting at 1.630 eV, and detecting at the maximum of the PL. The lines represent the best fit to a monoexponential decay, from which the "effective" spin-flip times $\tau_{\mathcal{P}}$ are obtained. The inset shows the initial degree of polarization as a function of carrier density, exciting at the lh exciton (1.643 eV).

ing carrier density has also been reported in the literature.[32] However, Damen *et al.* observed,[5] in a very high-quality sample, that $\tau_{\mathcal{P}}$ increase with ρ, which is at variance with our results. This disagreement may be due to the extremely high quality of that sample.

The importance of the screening of the Coulomb interaction is also revealed by the carrier-density dependence of the initial degree of polarization $\mathcal{P}(t_0)$, when exciting resonantly at the light-hole exciton, which is compiled in the inset of Fig. 8. At this excitation energy, both uncorrelated electron-hole pairs and excitons are created. The increase of $\mathcal{P}(t_0)$ with increasing ρ evidences the reduction of excitonic interaction, which leads to a cancellation of the free-carrier and excitonic contributions to $\mathcal{P}(t_0)$. A small decrease of $\tau_{\mathcal{P}}$ is also observed in this case, but reliable values of $\tau_{\mathcal{P}}$ cannot be obtained due to the small values of the polarization.

3. Detection-energy dependence

We have found that, at low temperatures, the polarization decay time depends strongly on the detection energy, and that this dependence disappears on increasing the temperature. These findings are shown in Fig. 9, together with the PL spectra recorded at a delay of 300 ps, for two different temperatures: 4 K, Fig. 9(a), and 70 K, Fig. 9(b). In both cases an initial carrier density of 2×10^{10} cm^{-2} was used, and the excitation was done 20 meV above the PL maximum.

We believe that the observed dependence of $\tau_{\mathcal{P}}$ on detection energy is a consequence of the influence of excitonic localization on spin-relaxation processes. However, due to the large difference in the spin-flip time of electrons and holes,[5] this dependence cannot arise from the enhancement in the hole spin-relaxation rate induced by localization (see Sec. IV B). Two different reasons can be invoked to explain this behavior: one, the dependence of the scattering time on excitonic localization; the second, the influence of localization on the coupling between $|+1\rangle$ and $|-1\rangle$ excitonic states.

As we have mentioned in Sec. IV B, the PL band at low temperatures is composed by the emission of localized excitons on different interface defects. The degree of localization of these excitons increases on moving towards the low-energy tail of the photoluminescence;[18] a concomitant increase of the momentum scattering time is expected due to the decrease of the diffusion constant, and, therefore, of the mobility of the excitons.[33] This effect influences the spin relaxation caused by the DP and exchange mechanisms in a similar way, decreasing the

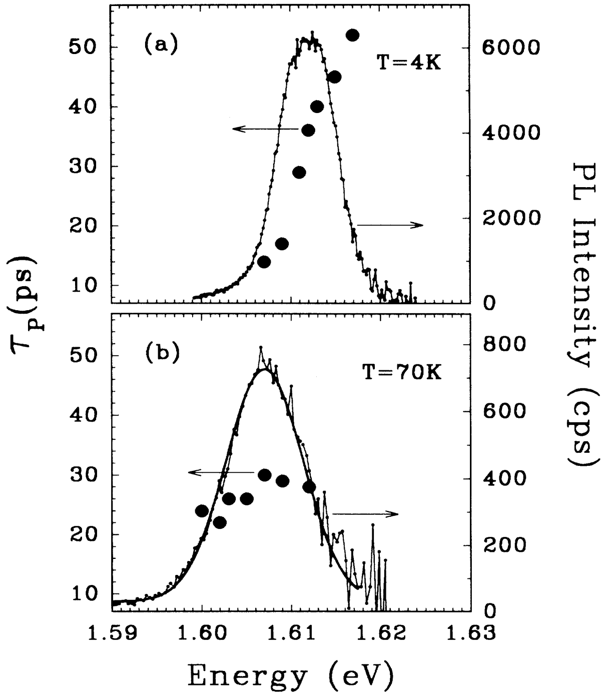

FIG. 9. Detection-energy dependence of the polarization decay time (left axes) for two different lattice temperatures: (a) 4 K and (b) 70 K (circles). The thin lines show the PL spectra at a delay of 300 ps (right axes). The thick line is the best fit to a Gaussian line shape.

spin-flip time, because in both cases $\tau_{\mathcal{P}}$ can be written as inversely proportional to the momentum relaxation time.[17,22]

The coupling between $|+1\rangle$ and $|-1\rangle$ excitonic states due to the long-range part of the exchange interaction is proportional to the square modulus of the exciton wave function at zero relative distance, $|\Phi_{1s(\mathrm{hh})}(0)|^2$. For free excitons, the exciton binding energy R_y^*, and $|\Phi_{1s(\mathrm{hh})}(0)|^2$ are directly proportional, and therefore an increase in binding energy produces a stronger coupling. For localized excitons, the relation between R_y^* and $|\Phi_{1s(\mathrm{hh})}(0)|^2$ depends on the specific characteristics of the localization center (for example, depth or lateral size), but if a similar dependence of $|\Phi_{1s(\mathrm{hh})}(0)|^2$ on R_y^* to that of free excitons holds, then an increase in binding energy should decrease the spin-flip time. Our arguments are only qualitative and do not yield the relative importance of the DP and exchange contributions to spin-flip processes; a complete detailed calculation would be necessary to distinguish which mechanism is more strongly affected by localization.

The assignment of localization as the origin of the dependence of $\tau_{\mathcal{P}}$ on detection energy is corroborated by the results obtained at 70 K. At that temperature we have found that the $\tau_{\mathcal{P}}$ dependence is strongly reduced [see Fig. 9(b)]. From cw measurements, we know that at temperatures higher than 40 K the Stokes shift vanishes, showing that the contribution of localized excitons to the PL diminishes. In fact, the photoluminescence spectrum at 70 K can be fitted to a Gaussian line shape with a full width at half maximum (FWHM) of 8±1 meV (solid thick line in the figure). This value is comparable, taking into account thermal broadening, to that obtained in very high-quality samples with negligible Stokes shifts even at low temperatures.[19] Therefore we believe that the emission band at 70 K can be attributed to an inhomogeneous distribution of free excitons. Since the momentum scattering time of the excitons will be similar for the whole distribution, the spin-flip time is expected to be almost independent of the detection energy, as is observed. The decrease of $\tau_{\mathcal{P}}$ at the maximum of the PL with increasing temperature is discussed in the next section.

4. Lattice-temperature dependence

The temperature dependence of the polarization decay time is shown in Fig. 10. The detection energy was set at the maximum of the PL and a difference of 20 meV between excitation and detection was kept for all temperatures. Two different temperature regimes are observed: for T lower than 40 K, the polarization decay time remains constant; for higher temperatures, $\tau_{\mathcal{P}}$ decreases with increasing T. The solid line represents the best fit to a power law, which gives a $T^{-2/5}$ dependence in the range $50 \leq T \leq 200$ K.

Let us discuss first the high-temperature behavior of $\tau_{\mathcal{P}}$ and assume that the DP interaction was the leading spin-flip mechanism. In this case, $\tau_{\mathcal{P}}^{-1}$ would depend on T as $T \times \tau^*(T)$ [see Eq. (1)]. We have not any direct measurement of τ^* on our sample, but if we use the available data in the literature, for temperatures above 50 K the momentum scattering time τ^* decreases with temperature approximately as T^{-2} (Refs. 34 and 35). Therefore the DP mechanism can be disregarded, because it would yield an increase in the spin-flip time with increasing temperature. This behavior is at variance with the one found in bulk semiconductors, where $(\tau_e^{\mathrm{DP}})^{-1}$ depends on temperature as $T^3 \times \tau^*(T)$, and where therefore the DP mechanism is found to be the dominant one at high temperatures.[3]

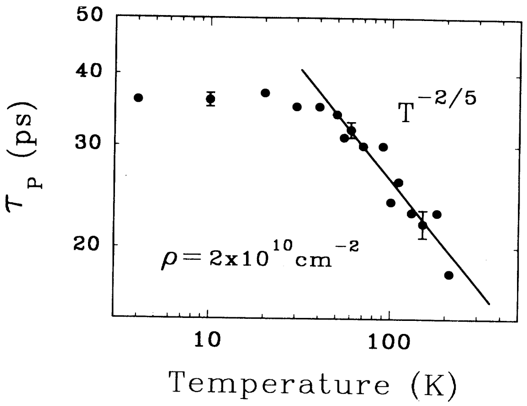

FIG. 10. Temperature dependence of the polarization decay time for an initial carrier density of 2×10^{10} cm^{-2}. The detection energy was set at the maximum of the PL and a difference of 20 meV between excitation and detection was kept for all temperatures. The solid line represents the best fit to a power law, which gives a $T^{-2/5}$ dependence in the range $50 \leq T \leq 200$ K.

For the case of the exchange interaction, in which the spin-relaxation time can be written as $\tau_{\mathcal{P}}^{-1} = \Omega_{\parallel}^2 \tau^*$,[17] one has to consider also the T dependence of the exchange coupling ($\Omega_{\parallel}$). With increasing T, the thermalized distribution of excitons gets wider and thus the mean wave vector of the excitons becomes larger. Since the coupling between $|+1\rangle$ and $|-1\rangle$ state is proportional to $\mathbf{K}$ [see Eq. (4)], $\Omega_{\parallel}$ would increase with temperature. However, a crude estimation of $\Omega_{\parallel}^2(T)$, averaging over the whole thermalized distribution, gives only a linear dependence with T. Therefore, taking into account that τ^* is proportional to T^{-2}, the overall result is that $\tau_{\mathcal{P}}$ should increase with temperature, in disagreement with the experimental findings.

In the low-temperature range ($4 \leq T \leq 40$ K), the temperature dependence of the momentum scattering time[34,35] would produce a decrease of $\tau_{\mathcal{P}}$ with increasing T for both the DP and exchange mechanisms. However, we believe that this effect is canceled by the enhancement of the free-exciton contribution to the PL, which increases the spin-flip relaxation time (see Sec. IV C 3). One could also think that the temperature independence in this range could originate from the fact that, at high carrier densities, the excitons could have a thermalized distribution with an effective temperature higher than the lattice temperature. However, this interpretation can be disregarded in the light of our results of Sec. IV A, which show that the decay and rise times are strongly dependent on T for an initial carrier density of 4×10^{10} cm^{-2}.

V. SUMMARY

We have investigated spin-relaxation processes in intrinsic GaAs QW's by varying the excitation and detection energy, the carrier density, and the lattice temperature. The studies have been done in a sample which displays a small Stokes shift but whose dynamical properties are analogous to those observed in very high-quality samples. The presence of the shift has allowed us to study the influence of excitonic localization on spin relaxation.

In the case of resonant excitation of hh excitons with $\mathbf{K}=0$, we have found a fast initial decay of the photoluminescence which is due to the removal of excitons from optically active states to dark states, and that, for holes correlated to electrons, the hole spin relaxation time is strongly dependent on excitonic localization. Excitonic localization also affects the spin relaxation of the exciton as a whole. This behavior can be explained from the theory of spin relaxation due to the DP mechanism and to the exchange interaction, but we are not able to draw conclusions about the relative importance of the two mechanisms.

We have found that valence-band mixing is responsible for the strong dependence of the initial degree of polarization on excitation energy. The dependence of the polarization decay time on excitation energy indicates that exchange interaction is the leading spin-relaxation mechanism at low temperatures. The measurements done with varying carrier density have shown the importance of screening and of the carrier scattering time in the determination of the spin-relaxation time.

Finally, we have observed two different regimes in the lattice-temperature dependence of the polarization decay time. We attribute the independence of τ_P at low temperatures as a consequence of the decrease of excitonic localization with temperature. The high-T dependence cannot be explained in a simple manner either by the DP mechanism or by the exchange interaction. A complete calculation of the spin relaxation considering the thermal distribution of excitons would be desirable to explain this behavior.

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