PHYSICAL REVIEW B **68**, 161309(R) (2003)

Single-hole spin relaxation in a quantum dot

T. Flissikowski, I. A. Akimov, A. Hundt, and F. Henneberger*
Humboldt Universität zu Berlin, Institut für Physik, Newtonstrasse 15, 12489 Berlin, Germany

(Received 19 June 2003; published 20 October 2003)

Using the photoluminescence of the trion feature as a monitor, we study experimentally the spin relaxation of the hole in self-assembled CdSe/ZnSe quantum dots. We observe two kinds of depolarization. The first one is due to an imperfect spin imprint of the circular photon polarization. The second transient depolarization is caused by the hole spin-flip in the Kramers degenerate trion doublet. At low temperature, the spin relaxation exhibits a slow component with a time constant longer than 10 ns. A considerable speedup takes place at higher temperature, reaching the sub nanosecond range at about 70 K. The activation energy is consistent with LO phonons.

DOI: 10.1103/PhysRevB.68.161309 PACS number(s): 78.66.Hf, 78.67.Hc, 78.20.Ls, 78.47.+p

Self-assembled quantum dots (QD's) have attracted a lot of attention during the past years as possible candidates for quantum information processing.[1] In this context, the carrier spin and its dynamics are of central interest. The discrete energy structure of QD's may give rise to spin-relaxation times much longer than for bulk semiconductors or quantum wells. So far, optical measurements have mostly addressed the exciton spin dynamics.[2–7] The fine structure of the QD exciton, comprising optically allowed and forbidden states, all split by the electron-hole exchange, leads to a complex multicomponent time scenario, where electron and hole contribution can be hardly separated. Much less is currently known on the spin relaxation of single carriers in QD's.

Charged QD's with resident carriers provide access to the separate spin dynamics of electrons and holes.[8–11] Recently, an electron-spin memory time of 15 ns has been deduced from ensemble data on *n*-doped InAs/GaAs QD structures.[9] As a consequence of the valence band substructure, the spin relaxation of holes is generally faster than for electrons.[12,13] In quantum wells, where heavy- and light-hole bands are split, the relaxation time can reach 1 ns.[14] To the best of our knowledge, no experimental data on the hole spin dynamics in single QD's is so far available. In this work, we study experimentally the spin flip of the hole in self-assembled CdSe/ZnSe QD's. Our concept is based on the photoluminescence (PL) from QD's charged with a single electron. Here, optical excitation creates a trion state consisting of one hole and two electrons. The total spin of the trion is half integer and its eigenstates are hence Kramers doublets degenerate in zero magnetic field. The trion ground state is a singlet state represented by two electrons in the first electron shell and one hole in the first heavy-hole shell. Due to the Pauli exclusion principle, the total spin of the electrons is zero, so that the resultant angular momentum of the trion is defined by that of the hole with projection of $j_z = \pm\frac{3}{2}$. There is no net electron-hole exchange as the contributions from the electrons with oppositely aligned spins cancel each other.[15] Radiative recombination of the trion leaves a single electron with $j_z = \pm\frac{1}{2}$ behind. The angular momentum rule demands $|\pm\frac{3}{2}\rangle \rightarrow \sigma^\pm + |\pm\frac{1}{2}\rangle$, with $\sigma^\pm$ denoting the respective circular light polarization. Therefore, the polarization of the emitted photon directly monitors the spin orientation of the hole, i.e., σ^+ for $+\frac{3}{2}$ and σ^- for $-\frac{3}{2}$, respectively. In what follows, we focus on the longitudinal relaxation time τ_{SF} associated with the spin flip in the Kramers degenerate doublet. An electron spin-flip is excluded, as it would lead to the trion triplet state located 70–80 meV on the high-energy side.[16] We emphasize that this situation is entirely different from the one of the exciton in uncharged QD's. Here, either hole or electron spin flip would create a dark state with slightly lower energy, not directly accessible in the experiment.

The CdSe/ZnSe QD samples were grown by molecular-beam epitaxy, using a thermal activation procedure.[17] Height and diameter of the pure CdSe core are about 2 nm and 5–10 nm, respectively, as revealed by transmission electron microscopy.[18] The samples are naturally *n* doped. In order to study individual QD's, mesa structures with an area down to $100\times 100\ \mathrm{nm}^2$ were prepared by electron beam lithography and wet chemical etching. For the magneto-PL measurements, the sample was placed in a split-coil cryostat capable of fields $B \leqslant 12$ T and excited with a cw Ar^+ laser ($\hbar\omega_{exc} = 2.54$ eV), somewhat above the wetting layer continuum edge. The PL signal was dispersed in a single monochromator with a linear dispersion of 0.24 nm/mm and detected with a nitrogen cooled charge coupled device matrix. The experiments were carried out in backward geometry with propagation direction of incident and emitted light parallel to the [001] growth axis (z axis). In time-resolved measurements, single mesas were optically selected by a microscope in a confocal arrangement. The sample was excited by the sum frequency of a Kerr-lens mode-locked Ti:sapphire laser and a synchronously pumped optical parametric oscillator. The pulses with a repetition rate of 76 MHz had a duration of 1.5 ps, a spectral full width at half maximum of 1.5 meV, and an energy density of 2 $\mu\mathrm{J/cm}^2$. The PL signal was dispersed in a double monochromator with 1.7 nm/mm linear dispersion in subtractive mode and detected by a multi-channel-plate photomultiplier. A time-correlated single-photon counting unit provided an overall time resolution of 80 ps. Circular polarization control was achieved by a λ/4 plate, placed both in the path of the (originally linearly) polarized excitation light as well as the PL signal. σ^+ or σ^- polarization of the PL was selected by rotation of a λ/2 plate in front of a Glan-Thomson prism introduced before the monochromator. The degree of circular polarization is defined as $\rho_c = (I_{\sigma^+} - I_{\sigma^-})/(I_{\sigma^+} + I_{\sigma^-})$, where I_{σ^+} and I_{σ^-} are

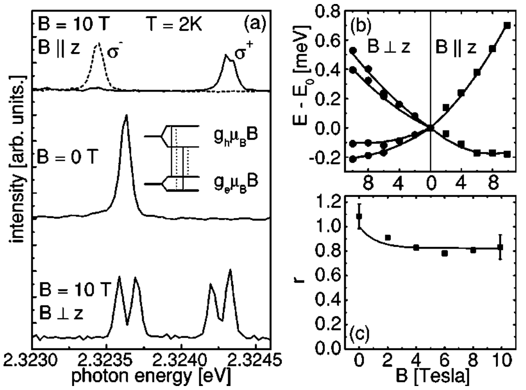

FIG. 1. (a) PL spectra from a single negatively charged QD under cw excitation at $B=0$ (middle) and $B=10$ T in Faraday (top) and Voigt (bottom) geometries (Inset: scheme of the optical transitions). (b) Fan charts. (c) Intensity ratio r between σ^+ and σ^- components in Faraday geometry. Solid line is a fit with Eq. 2.

the σ^+ and σ^- PL intensities, respectively, under σ^+ excitation.

First, we present low-temperature ($T=2$ K) magneto-PL data under nonresonant, linearly polarized cw excitation. Here, separation of the emission from $|\pm\frac{3}{2}\rangle$ is accomplished via the energy shift caused by the external field. Figure 1(a) summarizes typical PL spectra from a single QD measured at $B=0$ and $B=10$ T. In Voigt geometry ($B\perp z$), the single line observed at $B=0$ splits in four components, while a doublet of two circularly polarized lines occurs in Faraday geometry ($B\|z$) with σ^- (σ^+) for the low (high) energy component. The fan charts, depicting the line positions as a function of B, are presented in Fig. 1(b). After substraction of the overall diamagnetic shift, the g factors of electron and hole for the respective field geometry can be extracted from these plots. Observation of four lines in Voigt geometry results from the fact that a transverse magnetic field couples the electron as well as the hole spin so that all four trion transitions become optically allowed. Extrapolating the energy positions for each of the components down to $B=0$, we find no zero-field splitting, which prove the trionic nature of the emission line.[15,19,20] From the fan curves in Voigt geometry, we evaluate in-plane g factors for the electron of $g_{\mathrm{e},\perp}=1.1$ and for the hole of $g_{\mathrm{h},\perp}=0.2$, respectively.[21]

In longitudinal magnetic field, where the spin eigenstates are maintained, the PL doublet corresponds to the transitions $|\pm\frac{3}{2}\rangle\rightarrow\sigma^{\pm}+|\pm\frac{1}{2}\rangle$, already allowed at $B=0$. The field-induced splitting is now determined by the g factors along the quantization axis. Assuming that the electron g factor is isotropic, we find $g_{\mathrm{h},z}=2.6$, which allows one to estimate the energy splitting $\Delta E_{\mathrm{h}}=g_{\mathrm{h},z}\mu_{\mathrm{B}}B$ between the initial states of the recombination. Since the excitation is linearly polarized in this measurement, both states are addressed with equal probability (no optical orientation), while thermalization subsequently increases the $|-\frac{3}{2}\rangle$ occupation. The intensity yield of the PL lines provides hence a measure of τ_{SF}. The ratio $r=I_{\sigma^+}/I_{\sigma^-}$ is plotted versus B in Fig. 1(c). There is only a very weak variation up $B=10$ T, although, at this field strength, $\Delta E_{\mathrm{h}}=1.50$ meV is markedly larger than the thermal energy $k_{\mathrm{B}}T=0.34$ meV. This fact suggests slow thermalization and thus a long τ_{SF}. Denoting by $n_{\pm}$ the occupation of the $|\pm\frac{3}{2}\rangle$ state, the two-level rate equations read

$$\dot{n}_{\pm}=g_{\pm}-\frac{n_{\pm}}{\tau}\mp\frac{n_{+}}{\tau_{\mathrm{SF}}}\pm\exp\left(-\frac{\Delta E_{\mathrm{h}}}{k_{\mathrm{B}}T}\right)\frac{n_{-}}{\tau_{\mathrm{SF}}}, \qquad (1)$$

where τ is the radiative lifetime of the trion and $g_{\pm}$ denotes the respective pump rate. For steady-state conditions and $g_{+}=g_{-}$, it follows

$$r=\frac{n_{+}}{n_{-}}=\frac{1+\dfrac{2\tau}{\tau_{\mathrm{SF}}}\exp\left(-\dfrac{\Delta E_{\mathrm{h}}}{k_{\mathrm{B}}T}\right)}{1+\dfrac{2\tau}{\tau_{\mathrm{SF}}}}. \qquad (2)$$

A fit of the data with this formula yields $\tau/\tau_{\mathrm{SF}}=(0.11\pm0.06)$. In what follows, we present more direct measurements of τ_{SF} in the time domain.

Excitation with σ^+ polarized pulses creates predominantly trions with hole spin $j_z=\frac{3}{2}$, as long as the excitation energy is sufficiently below the trion triplet state. Analyzing the depolarization of the emission, one can determine τ_{SF}. Strictly resonant excitation of the ground state is faced with extreme stray light problems. For this reason, we used LO-phonon assisted excitation by tuning the photon energy 28 meV above the groundstate transition. Time- and polarization-resolved data for a single QD at $T=5$ K are summarized in Fig. 2. The upper part depicts the PL transients for σ^+ and σ^- detection. During the first 150 ps, the σ^+ signal is still spoiled by stray light and will be hence disregarded in the further analysis. Beyond this range, both signals decay in very good approximation single exponentially. In the lower part of the figure, the degree of circular

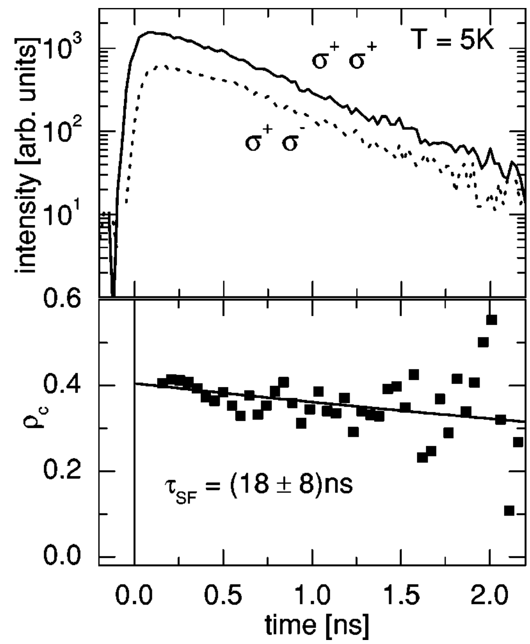

FIG. 2. Upper part: Decay transients of the trion PL under LO-phonon-assisted pulsed σ^+ excitation for σ^+ and σ^- detection ($T=5$ K). Lower part: Time dependence of the degree of circular polarization ρ_c (squares). The solid line is a fit with Eq. 3.

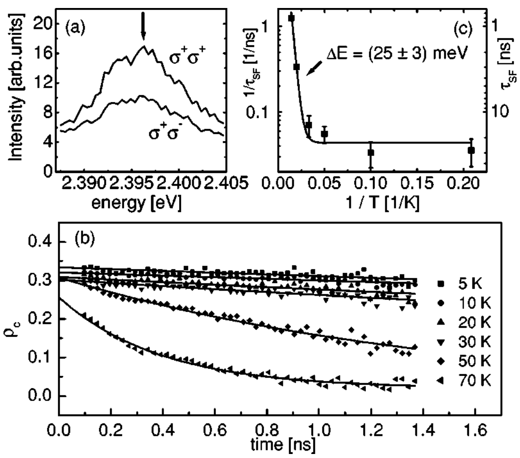

FIG. 3. (a) Time integrated PL spectra measured in σ^+ and σ^- polarization from an ensemble of QD's under σ^+ pulsed excitation one LO-phonon energy above the arrow. (b) Time dependence of ρ_c taken in a 0.5 meV window around the arrow. Solid curves correspond to an exponential fit with Eq. (3). (c) Temperature dependence of spin-relaxation rate $1/\tau_{SF}$. Solid curve is a fit with $[0.05+42\cdot\exp(-\Delta E/k_B T)]$ ns^{-1}.

polarization ρ_c is shown. Consistent with the magneto-PL results, we only find very little depolarization within the trion lifetime. Note, however, that the initial polarization degree, observed when the experimental data start to be meaningful, is only about 0.4. Under linearly polarized excitation, the PL signal exhibits no linear polarization component within the experimental accuracy of ± 0.05. Solving the rate equations now in the transient case and $\Delta E_h = 0$ yields for the degree of circular polarization

$$\rho_c = \rho_0 \exp\left(-\frac{2t}{\tau_{SF}}\right), \tag{3}$$

where ρ_0 is the initial value. From the fit of the data in Fig. 2 we obtain $\tau_{SF}=(18\pm 8)$ ns and $\tau = 500$ ps. These numbers compare reasonably well with the ratio τ/τ_{SF} from the magneto-PL.

For a better signal-to-noise ratio, the temperature dependence of the hole spin flip was studied on a mesa with 400-μm^2 size. Here, the emission lines from single QD's cannot be separated. The excitation photon energy is tuned to the maximum of the inhomogeneously broadened PL band occurring for continuum excitation. The ensemble includes charged and uncharged QD's, however, the linearly polarized excitons do not contribute to the decay of ρ_c.[1,3,4,6] The PL band present in this case [see Fig. 3(a)] has a spectral width of 10 meV and its maximum is located 28 meV below the excitation photon energy. Excitation via 1-LO-phonon assistance is hence predominant, resembling the situation for the single-QD measurements. Across the whole band, the polarization degree is positive, however, with larger values at the center. Obviously, acoustical phonons, coming into play at the edges, are a source of further depolarization. In Fig. 3, the time-resolved polarization degree taken at the band maximum is plotted for different temperatures (5–70 K). The low-temperature curves ($T<30$ K) are consistent with the results for the single-trion PL, demonstrating that the ensemble data are not distorted by statistical properties. The spin-flip times that follow from the transients are summarized in Fig. 3(c). A marked shortening sets on at higher temperatures so that a value of only $\tau_{SF}=0.8$ ns is reached at 70 K. The data points follow closely an Arrhenius plot with an activation energy of $\Delta E=(25\pm 3)$ meV.

In general, the spin dynamics of the hole is governed by the substructure of the valence band. At $\vec{k}\neq 0$, none of the states is a true eigenfunction of the angular projection operator $\mathbf{J}_z$. For a QD, this fact translates in a hole wave function of the form $\psi=\Sigma\varphi_{j_z}(\vec{r})|j_z\rangle$, where we restrict ourselves in what follows to the heavy- and light-hole bands $(j_z=\pm\frac{3}{2},\pm\frac{1}{2})$. PL excitation measurements have uncovered a set of excited trion states, starting with a feature separated by $\Delta=40$ meV from the ground-state transition.[16] This feature is due to excitation of the second hole shell, presumably associated with the first light-hole state. The next zero-phonon resonance, related to the second electron shell, is already shifted by 80 meV to higher energies. In view of the large energy separations, the leading contribution to ψ arises in first order from the light-hole ground state. Denoting by $\varphi_0^{hh/lh}$ the zeroth-order envelope functions, this yields for the trion ground state $\psi_\pm=\varphi_0^{hh}|\pm\frac{3}{2}\rangle-\varphi_0^{lh}(I^\pm|\mp\frac{1}{2}\rangle+R^\pm|\pm\frac{1}{2}\rangle)/\Delta$. $I^\pm$ and $R^\pm$ are the $\mathbf{k}\cdot\mathbf{p}$ matrix elements of φ_0^{hh} and φ_0^{lh}.[22] Two different sources for spin coupling arise from these wavefunctions. First, the spin imprint of the circular photon polarization is not perfect; i.e., a σ^+ photon can excite ψ_+ from an initial spin-up electron, while ψ_- is addressed for spin down. This softening of the selection rule is caused by the parity-conserving term $\sim I^\pm$. Second, the admixtures $\sim R^\pm$ mediate a flip between ψ_+ and ψ_-. This contribution of the heavy-light-hole coupling does not conserve parity. Note that interactions V, not depending on the carrier spin, then provide a nonzero scattering matrix element $\langle\psi_+|V|\psi_-\rangle$.

Our experimental findings reveal both kinds of spin coupling. The fact that no linearly polarized PL component is observed signifies that the light-hole admixture in the zero-phonon trion ground state $|\psi_\pm,0\rangle$ is indeed small. However, the trion-LO-phonon state $|\psi_\pm,1\rangle$, where the QD is excited, is markedly closer to the light-hole level ($\Delta=12$ meV). The mixing coefficients, $I^\pm/\Delta$ and $R^\pm/\Delta$, are thus by a factor of about 4 larger and their squares even by more than an order of magnitude. The σ^+ pulse hence creates a significant ψ_- portion. During relaxation, $|\psi_\pm,1\rangle$ is converted in the practically pure angular momentum state $|\psi_\pm,0\rangle\approx\varphi_0^{hh}|\pm\frac{3}{2}\rangle$, which subsequently gives rise to both σ^+ and σ^- polarized PL components. This depolarization, involving no flip between ψ_+ and ψ_-, defines a temperature-independent contribution to the initial drop of ρ_c down to 0.4 before we observe the first evaluable photons after about 150 ps. A partial loss of polarization during the conversion from the one- to the zero-LO-phonon state has been also observed for the exciton in uncharged QD's.[4,6]

The lifetime of the trion-LO-phonon complex is limited by the decay of the optical mode, most probably in acoustical phonons. The absence of any noticeable PL yield[16] indicates that this lifetime is at maximum a few 10 ps. The second much slower depolarization seen in the low-temperature PL transients is therefore related to scattering from ψ_+ to ψ_- in the trion ground state. The spin-flip times are here longer than 10 ns. Hyperfine interaction with the nuclear spins, invoked to define a limit for the electron-spin-flip in QD's,[23] is by far less efficient for holes, because of their *p*-type Bloch functions.[24] Flip by a spin-independent interaction requires parity breaking so that $R^{\pm} \neq 0$. An irregular QD shape or strain can be a reason for this. Otherwise, envelope functions of excited states with larger energy separation have to be included in the wave functions. In addition, the resultant spin-flip matrix element is of second order ($\sim I^{\pm} R^{\mp}$) in the band mixing. Therefore, while we can currently not specify the actual low-temperature mechanism (defects, disorder, phonons, etc.), the above considerations demonstrate that the observation of very long hole spin-flip times is in no contradiction to the general expectation. The somewhat shorter τ_{SF} obtained from the magneto-PL data might indicate a more efficient spin flip when the degeneracy of the doublet is removed, enabling direct transition with acoustical phonons.

The speedup at higher temperatures has an activation energy consistent with LO phonons. Increasing occupation of the one-phonon complex has the consequence that a part of the spin flip takes place in this state. As noted above, the heavy-light-hole coupling is stronger here. However, more importantly, the bandwidth of the one-LO resonance is 8 meV,[16] presumably due to disorder fluctuations of the phonon energy. The hole is thus more heavily subject to scattering with the consequence of also distinctly shorter spin-flip times than in the ground state.

In conclusion, we have observed two kinds of depolarization associated with the hole spin in a QD. Both are related to heavy-light-hole coupling. The first one is caused by an imperfect spin imprint of the circular photon polarization. This depolarization is enhanced in our measurements, as the QD is excited close to the light-hole shell. It can be thus strongly suppressed by resonant excitation of the trion ground state. The low-temperature spin flip in the degenerate hole doublet exhibits a component with a time constant longer than 10 ns. This is a consequence of the large separations between the discrete energy levels in QD's reducing strongly the band mixing. At higher temperature, along with the population of the LO-phonon modes, the spin flip becomes increasingly rapid and reaches the subnanosecond range at about 70 K. This is mostly a result of the relatively large scattering rates in trion-LO-phonon state. Reduction of those rates is the key for achieving long spin-flip times at elevated temperatures.

The authors thank S. Rogaschewski for the lithographic etching. This work was supported by the Deutsche Forschungsgemeinschaft by Project No. He 1939/11-3.

*Electronic address: henne@physik.hu-berlin.de

[1] D. Gammon and D.G. Steel, Phys. Today **55** (10), 36 (2002), and references therein.

[2] H. Nickolaus, H.-J. Wünsche, and F. Henneberger, Phys. Rev. Lett. **81**, 2586 (1998).

[3] M. Paillard, X. Marie, P. Renucci, T. Amand, A. Jbeli, and J.M. Gérard, Phys. Rev. Lett. **86**, 1634 (2001).

[4] T. Flissikowski, A. Hundt, M. Lowisch, M. Rabe, and F. Henneberger, Phys. Rev. Lett. **86**, 3172 (2001).

[5] J.A. Gupta, D.D. Awschalom, Al.L. Efros, and A.V. Rodina, Phys. Rev. B **66**, 125307 (2002).

[6] M. Scheibner, G. Bacher, S. Weber, A. Forchel, Th. Passow, and D. Hommel, Phys. Rev. B **67**, 153302 (2003).

[7] E. Tsitsishvili, R.v. Baltz, and H. Kalt, Phys. Rev. B **67**, 205330 (2003).

[8] R.I. Dzhioev, B.P. Zakharchenya, V.L. Korenev, P.E. Pak, D.A. Vinokurov, O.V. Kovalenko, and I.S. Tarasov, Fiz. Tverd. Tela **40**, 1745 (1998) [Phys. Solid State **40**, 1587 (1998)].

[9] S. Cortez, O. Krebs, S. Laurent, M. Senes, X. Marie, P. Voisin, R. Ferreira, G. Bastard, J.M. Gérard, and T. Amand, Phys. Rev. Lett. **89**, 207401 (2002).

[10] I.V. Ignatiev, I.Ya. Gerlovin, S.Yu. Verbin, I.A. Yugova, and Y. Masumoto, Physica E (Amsterdam) **17**, 361 (2003).

[11] M. Sénès, X. Marie, B. Liu, and T. Amand, in *Proceedings of the 26th Conference on the Physics of Semiconductors, Edinburgh,* UK, edited by A.R. Long and J.M. Davies (Institute of Physics, Bristol, 2002).

[12] *Optical Orientation*, edited by F. Meier and B. P. Zakharchenya (North-Holland, New York, 1984).

[13] L. Viña, J. Phys.: Condens. Matter **11**, 5929 (1999), and references therein.

[14] Ph. Roussignol, P. Rolland, R. Ferreira, C. Delalande, G. Bastard, A. Vinattieri, J. Martinez-Pastor, L. Carraresi, M. Colocci, J.F. Palmier, and B. Etienne, Phys. Rev. B **46**, 7292 (1992).

[15] I.A. Akimov, A. Hundt, T. Flissikowski, and F. Henneberger, Appl. Phys. Lett. **81**, 4730 (2002).

[16] I.A. Akimov, A. Hundt, T. Flissikowski, P. Kratzert, and F. Henneberger, Physica E (Amsterdam) **17**, 31 (2003).

[17] M. Rabe, M. Lowisch, and F. Henneberger, J. Cryst. Growth **184/185**, 248 (1998).

[18] D. Litvinov, A. Rosenauer, D. Gerthsen, P. Kratzert, M. Rabe, and F. Henneberger, Appl. Phys. Lett. **81**, 640 (2002).

[19] M. Bayer, G. Ortner, O. Stern, A. Kuther, A.A. Gorbunov, A. Forchel, P. Hawrylak, S. Fafard, K. Hinzer, T.L. Reinecke, S.N. Walck, J.P. Reithmaier, F. Klopf, and F. Schäfer, Phys. Rev. B **65**, 195315 (2002); J.G. Tischler, A.S. Bracker, D. Gammon, and D. Park, *ibid.* **66**, 081310 (2002).

[20] J. Puls, M. Rabe, H.-J. Wünsche, and F. Henneberger, Phys. Rev. B **60**, 16 303 (1999).

[21] The *g* factors have been discussed in detail in Ref. 20 and in V.D. Kulakovskii, G. Bacher, R. Weigand, T. Kümmell, A. Forchel, E. Borovitskaya, K. Leonardi, and D. Hommel, Phys. Rev. Lett. **82**, 1780 (1999).

[22] D.A. Broido and L.J. Sham, Phys. Rev. B **31**, 888 (1985).

[23] A. Khaetskii, D. Loss, and L. Glazman, Phys. Rev. B **67**, 195329 (2003).

[24] E.I. Gryncharova and V.I. Perel', Fiz. Tekhn. Poluprovodn. **11**, 1697 (1977) [Sov. Phys. Semicond. **11**, 997 (1977)].