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Charged excitons in ZnSe-based quantum wells

G. V. Astakhov
A. F. Ioffe Physical-Technical Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia

D. R. Yakovlev
A. F. Ioffe Physical-Technical Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia and Physikalisches Institut der Universität Würzburg, 97074 Würzburg, Germany

V. P. Kochereshko
A. F. Ioffe Physical-Technical Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia

W. Ossau, J. Nürnberger, W. Faschinger, and G. Landwehr
Physikalisches Institut der Universität Würzburg, 97074 Würzburg, Germany

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We report on magneto-optical studies of ZnSe/(Zn,Mg)(S,Se) quantum wells with *n*-type and *p*-type modulation doping. Negatively and positively charged excitons related to the heavy-hole exciton states are found and identified by their polarization properties. Negatively charged excitons formed with light-hole exciton states are observed. Their binding energy is about 20% less than that related to the heavy-hole exciton. The exciton and trion parameters (radiative and nonradiative dampings) are determined. [S0163-1829(99)50136-7]

The existence of charged exciton complexes (trions) in semiconductors has been predicted by Lampert in 1958.[1] In analogy with charged hydrogen ions H^- and $H_2{}^+$ the negatively charged exciton (X^-), consisting of two electrons and one hole, and the positively charged exciton (X^+), formed by two holes and one electron, have been suggested. However, the first clear experimental proof of the existence of negatively charged excitons has been given only quite recently in 1993. Kheng *et al.* reported the observation of X^- states in CdTe-based quantum well (QW) structures with a two-dimensional electron gas (2DEG) of low density.[2] The calculation of the binding energy of the X^- complex gave for bulk material a rather small value (about 5% of exciton Rydberg energy), which prevented its experimental observation in three-dimensional (3D) systems. However, a reduction of the dimensionality to two dimensions strongly enhances the trion stability and increases its binding energy up to 20–45 % of the Rydberg energy. In recent years negatively charged excitons have been studied intensively in CdTe- and GaAs-based QW's.[3,4] The observation of positively charged excitons has also been reported for these structures.[5–8]

The trion binding energy can be enhanced not only by a reduction of the dimensionality but also by choosing another material system. A promising material is ZnSe with an exciton binding energy of 20 meV, which is considerably larger than that of GaAs (4.2 meV) or CdTe (10 meV). The technique of molecular-beam epitaxy (MBE) is well developed for the growth of ZnSe-based QW structures due to the work on blue-green emitting laser diodes.[9] However, most of the structures grown so far contain (Zn,Cd)Se QW's and ZnSe barriers. In these structures the exciton resonances are broadened significantly due to alloy fluctuations, which makes high-resolution optical spectroscopy of exciton and trion states very difficult. We are aware of one publication on X^- states in (Zn,Cd)Se/ZnSe QW's only.[10] Very recently the growth of high-quality lattice-matched ZnSe/(Zn,Mg)(S,Se) QW's allowed the observation of exciton lines with an inhomogeneous broadening smaller than 1 meV.[11,12] In this paper we report on magneto-optical studies of negatively and positively charged excitons in ZnSe/(Zn,Mg)(S,Se) QW's. Trion states related to both heavy-hole and light-hole excitons were found and analyzed.

ZnSe/$Zn_{0.89}Mg_{0.11}S_{0.18}Se_{0.82}$ single QW (SQW) structures were grown by MBE on (100) GaAs substrates. A special deposition of Zn by atomic-layer epitaxy was used for the growth start of a 200-Å ZnSe buffer layer on GaAs. ZnSe SQW's were located between $Zn_{0.89}Mg_{0.11}S_{0.18}Se_{0.82}$ barriers of 1000- and 500-Å thickness. A total band-gap discontinuity of 200 meV between the QW and the barrier materials is distributed about equally between the conduction- and valence-band edges. Here we report results for three structures. The first one is nominally undoped with a residual electron concentration of $n_e \leqslant 10^{10}\,\mathrm{cm}^{-2}$ in the 80-Å SQW. This low value is possible because of the weak *n*-type background conductivity of the barriers. The second structure with an 80-Å SQW has an electron concentration of $n_e = 9 \times 10^{10}\,\mathrm{cm}^{-2}$, it was achieved by modulation doping with a 30-Å-thick, Cl doped layer (donor concentration of $5 \times 10^{17}\,\mathrm{cm}^{-3}$) separated from the QW by a 100-Å-thick spacer. The third sample with a 120-Å SQW was *p*-type doped with nitrogen (RF plasma cell at a power of 350 W and a background pressure of 5×10^{-6} Torr). In this specimen, symmetric modulation doping was achieved by uniform doping of the barriers excluding 30-Å-thick spacer layers. The concentration of the two-dimensional hole gas (2DHG) in the QW is about $n_h \approx 3 \times 10^{10}\,\mathrm{cm}^{-2}$. Photoluminescence (PL) and reflectivity spectra were measured at 1.6 K and in magnetic fields up to 7.5 T applied perpendicular to the QW plane (Faraday geometry). Circularly polarized light

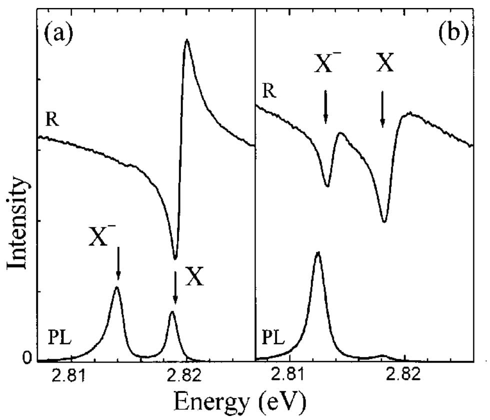

FIG. 1. Photoluminescence and reflectivity spectra of 80-Å $ZnSe/Zn_{0.89}Mg_{0.11}S_{0.18}Se_{0.82}$ QW's with different electron concentration in the QW's: (a) $n_e \leqslant 10^{10}$ cm^{-2}, excitonic parameters $\Gamma_0(X_{hh}) = 210$ μeV and $\Gamma(X_{hh}) = 0.38$ meV; (b) $n_e = 9 \times 10^{10}$ cm^{-2}, $\Gamma_0(X_{hh}) = 180$ μeV, $\Gamma(X_{hh}) = 0.7$ meV, $\Gamma_0(X^-_{hh}) = 67$ μeV, and $\Gamma(X^-_{hh}) = 0.6$ meV.

was analyzed by using achromatic quarter-wave plates. The signal was dispersed by a 1-m spectrometer and detected by a charge-coupled device.

In Fig. 1 the spectra obtained from nominally undoped and *n*-type QW's are compared. A single strong resonance is observed in the reflectivity spectrum at an energy of 2.8195 eV for the undoped QW, which corresponds to the 1*s* state of the heavy-hole exciton (detailed identification of the optical resonances by means of magneto-optics in fields up to 20 T was reported in Ref. 12). A procedure described in Ref. 13 was used to fit the reflectivity spectra and to deduce the excitonic parameters like radiative damping Γ_0, which corresponds to the exciton oscillator strength, and the nonradiative damping Γ to which inhomogeneous broadening and exciton scattering mechanisms contribute. The parameters determined are listed in the caption of Fig. 1. For the undoped structure [see Fig. 1(a)] one can recognize a weak feature 4.8 meV below the exciton resonance, i.e., at an energy where the bound exciton state is expected. Contrary to the reflectivity spectrum, in the PL spectrum the bound exciton (X^-) line is stronger than the excitonic one (X). The reason is that the strength of exciton or trion resonances in reflectivity are determined by the respective density of states, but the PL intensity is contributed additionally by a state occupation factor. At low temperatures the residual electrons and photogenerated excitons are thermalized into the same locations corresponding to minima of the potential fluctuations in the QW. As a result the probability of the X^- formation increases, which is visualized in turn by strong intensity of X^- luminescence in respect to the exciton one.

With the increase of the electron concentration of about 9×10^{10} cm^{-2} the X^- line becomes dominant in PL spectrum [see Fig. 1(b)]. But really drastic changes are observed in the reflectivity spectra, where a strong resonance with an oscillator strength of 37% [$\Gamma_0(X^-_{hh}) = 67$ μeV] of the excitonic one [$\Gamma_0(X_{hh}) = 180$ μeV] is visible at an energy of 2.813 eV. This observation allows unambiguously to assign this resonance to the negatively charged exciton state. We stress here that in reflectivity spectra only real resonances contributing to the dielectric function (with a sufficiently large density of

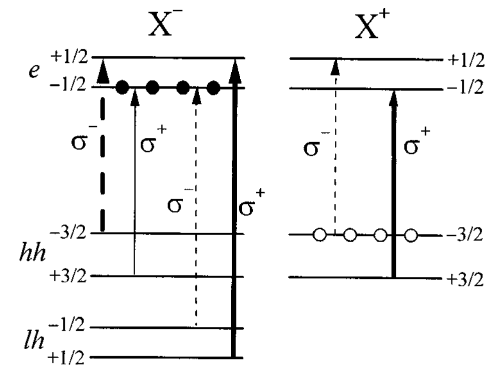

FIG. 2. Scheme of the optical transitions in ZnSe-based QW's for the creation of charged excitons in the cases of completely polarized 2DEG (shown by closed circles) and 2DHG (open circles) induced by external magnetic fields. Optically active circular polarized transitions are shown by arrows. The thick arrows represent the transitions in which the trion formation is allowed.

states) are detectable. The binding energy of the X^- state defined as the energy difference between X^- and X is 5.0 meV. It amounts to 17% of the exciton binding energy in the QW, the value of which 30 meV was determined from the fan chart of the magnetoexciton.[12]

The strong polarization of the X^- absorption in magnetic fields is a fingerprint of the trion that allows to distinguish clearly trion resonances from excitonic ones.[2] This is due to the singlet spin structure of the trion ground state, i.e., the spins of the two electrons involved in the X^- complex are oriented antiparallel. As a result, when a 2DEG is totally polarized by a magnetic field the X^- state can be excited optically only for one circular polarization [namely, σ^- polarization in ZnSe-based QW's with a positive electron g factor $g_e = +1.14$ (Ref. 14–16)]. A scheme of the optical transitions responsible for the X^- excitation in strong magnetic fields is presented in Fig. 2. Spin-split states of the bottom of the conduction band and the top of the valence band are shown. (The light-hole states in the studied QW's are split off to higher energies due to quantum-confinement and strain effects.) Arrows indicate optical transitions, when the absorbing light removes an electron from the valence band into the conduction band and forms an exciton. Exciton generation in a quantum well containing 2D electrons results in the direct excitation of X^-. Heavily and lightly drawn arrows mark the allowed and forbidden transitions for the excitation of X^- in its ground (singlet) state, when the 2DEG is polarized, i.e., all 2D electrons occupy the $-\frac{1}{2}$ spin sublevel of the lowest Landau level.

At 7.5 T the X^-_{hh} transition in the reflectivity spectra is totally polarized (see Fig. 3). Its oscillator strength becomes two times stronger in σ^- polarization, in comparison with the zero field value, and vanishes for σ^+ polarization keeping the integral oscillator strength $\Gamma_0^+(X^-_{hh}) + \Gamma_0^-(X^-_{hh}) = 135$ μeV constant. The degree of polarization of the trion transition calculated as $P_c = (\Gamma_0^+ - \Gamma_0^-)/(\Gamma_0^+ + \Gamma_0^-)$ is shown in the inset of Fig. 3 by circles. The equilibrium polarization of a nondegenerate 2DEG, calculated with the Boltzmann distribution, $g_e = +1.14$ and $T = 1.6$ K, is traced by a solid line. Experimental points coincide well with the line at fields above 3.7 T, which evidences that the temperature of the

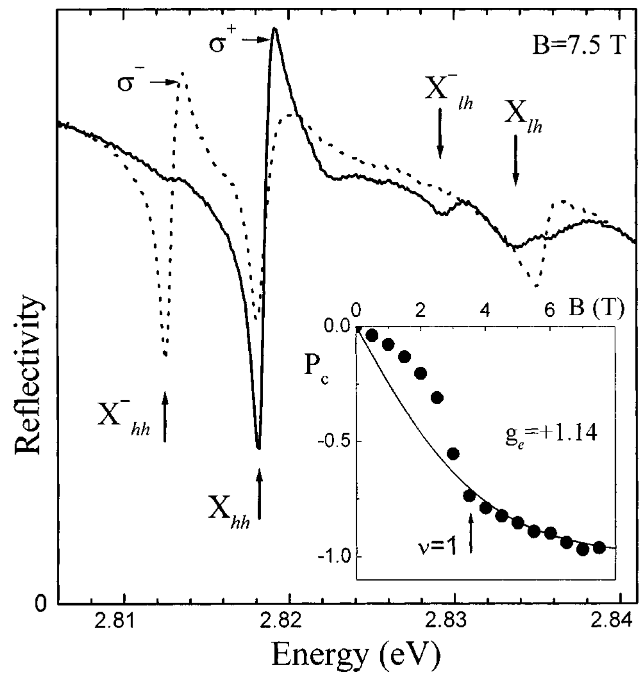

FIG. 3. Reflectivity spectra of an 80-Å $ZnSe/Zn_{0.89}Mg_{0.11}S_{0.18}Se_{0.82}$ QW (exciton line in the barrier at 2.99 eV) with $n_e=9\times10^{10}\,\mathrm{cm}^{-2}$ detected in different polarizations at a magnetic field of 7.5 T. Strongly polarized resonances of negatively charged excitons related to the heavy-hole (X_{hh}^-) and the light-hole (X_{lh}^-) excitons are marked by arrows. The inset shows the polarization degree of the X_{hh}^- line: circles are experimental points and the line represents the calculation based on the Boltzmann distribution with $g_e=+1.14$ at $T=1.6\,\mathrm{K}$.

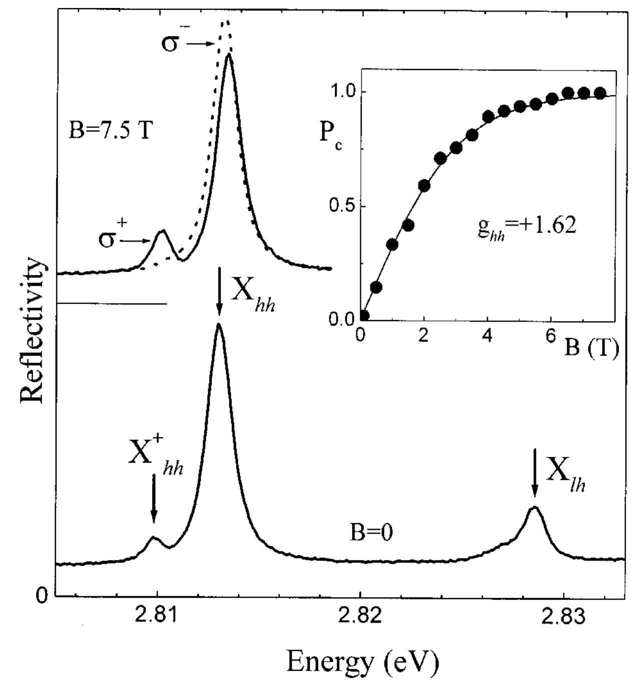

FIG. 4. The reflectivity spectra of a 120-Å $ZnSe/Zn_{0.89}Mg_{0.11}S_{0.18}Se_{0.82}$ QW with $n_h\approx3\times10^{10}\,\mathrm{cm}^{-2}$ measured at magnetic fields of 0 and 7.5 T. The line of the positively charged exciton (X_{hh}^+) is strongly polarized in magnetic fields. The inset shows the polarization degree of the X_{hh}^+ line: circles are experimental points and the line represents the calculation based on the Boltzmann distribution with $g_{\mathrm{hh}}=+1.62$ at $T=1.6\,\mathrm{K}$.

2DEG in the QW equals a lattice temperature of 1.6 K. Deviation from the Boltzmann distribution in low magnetic fields occurs for filling factors $\nu>1$. In this case Fermi-Dirac statistics describe the polarization properties of the 2DEG. We conclude from the inset of Fig. 3 that the condition $\nu=1$ is achieved at a magnetic field of 3.7 T. This, in turn, allows to determine the concentration of the 2DEG $n_e=\nu eB/hc=9\times10^{10}\,\mathrm{cm}^{-2}$ (details of this optical method of measuring carrier density in QW's will be published elsewhere).

In magnetic fields the heavy-hole exciton resonance (X_{hh}) in reflectivity spectra for the undoped QW's shows a weak diamagnetic shift and Zeeman splitting for the two spin components with an excitonic g factor $g_{\mathrm{exc}}=+0.38$ in an 80-Å-thick QW. The amplitudes of the exciton reflectivity lines detected in two circular polarizations are equal in the structure with $n_e\leqslant10^{10}\,\mathrm{cm}^{-2}$. However, a considerable polarization with a sign opposite to the polarization of the X_{hh}^- line shows up when n_e approaches a value of $9\times10^{10}\,\mathrm{cm}^{-2}$ (see Fig. 3). We believe that this polarization is caused by the effect of spin-dependent scattering of excitons with 2DEG electrons (for details see Ref. 17). We would like to stress here that for magnetic fields up to 7.5 T the radiative damping $\Gamma_0(X_{\mathrm{hh}})$ is kept equal for both polarizations $\Gamma_0^+(X_{\mathrm{hh}})=\Gamma_0^-(X_{\mathrm{hh}})=180\,\mu\mathrm{eV}$ and that the exciton line shapes differ due to the nonradiative broadening, which is spin dependent [$\Gamma^+(X_{\mathrm{hh}})=0.33\,\mathrm{meV}$ and $\Gamma^-(X_{\mathrm{hh}})=0.75\,\mathrm{meV}$ at 7.5 T].

Let us turn now to the light-hole exciton transition. It is obvious from the level scheme in Fig. 2 that X^- transitions associated with a heavy-hole exciton and a light-hole exciton should appear in the reflectivity spectrum in opposite polarizations. We indeed observe this experimentally (which can be seen by the solid line in Fig. 3). The X_{lh}^- transition is observed at 7.5 T as a clearly resolved resonance 4.4 meV below the energy of the light-hole exciton. The binding energy of X_{lh}^- is about 20% smaller than that of X_{hh}^-, which is 5.5 meV at 7.5 T. The radiative damping $\Gamma_0^+(X_{\mathrm{lh}}^-)=16\,\mu\mathrm{eV}$ of X_{lh}^- is about an order of magnitude less than that for the X_{hh}^- state. Such a large difference is somewhat surprising as the radiative damping for the heavy-hole and light-hole excitons differs only by a factor of about 2 [$\Gamma_0(X_{\mathrm{hh}})=180\,\mu\mathrm{eV}$ and $\Gamma_0(X_{\mathrm{lh}})=80\,\mu\mathrm{eV}$]. Further studies are required to clarify this problem. To the best of our knowledge no detailed investigation of X_{lh}^- states has been reported so far. Trions associated with light-hole excitons were observed in PL excitation spectra of GaAs/(Al,Ga)As QW's,[3] and in the reflectivity spectra of monomolecular CdTe islands.[18] In both cases the X_{lh}^- binding energy was very close to that of X_{hh}^-. Numerical calculations, performed by Stebe *et al.*[19] for GaAs QW's do not account for the modification of the in-plane effective mass in the valence band and, therefore, are not suitable for quantitative comparison with experimental data.

In Fig. 4 reflectivity spectra for a 120-Å-thick SQW with a low-density 2DHG with $n_h\approx3\times10^{10}\,\mathrm{cm}^{-2}$ are shown. A line of the positively charged exciton with a binding energy of 3.1 meV is observed in the spectrum. Its identification is based on the polarization properties of the X_{hh}^+ transition. Similar to the X_{hh}^- the X_{hh}^+ line is totally polarized in magnetic fields above 6 T. The signs of the polarization of the X_{hh}^- and X_{hh}^+ lines are opposite to each other, which is in accordance with the scheme of Fig. 2. The magnetic-field dependence of the X_{hh}^+ polarization degree (see circles in the inset of Fig. 4) coincides remarkably well with a calculation based on the Boltzmann distribution and a heavy-hole g factor $g_{hh} = +1.62$. This g factor value was deduced from the measured values $g_{exc} = +0.48$ and $g_e = +1.14$,[14] by means of the equation $g_{hh} = g_{exc} + g_e$.[15]

The value of the X_{hh}^+ binding energy of 3.1 meV is close to that for the X_{hh}^- taken from the interpolation between the data points for the 80-Å-thick QW (5.0 meV) and the 200-Å-thick QW (2.2 meV). This finding is in agreement with the results reported for QW structures based on GaAs,[6–8] CdTe,[5] and (Cd, Mn)Te.[20] The X^+ associated with the light-hole exciton was not detectable in our structures most probably due to the low hole concentrations.

Additionally to the negatively charged excitons the combined processes, which are typical for excitons interacting with a low-dense 2DEG, were observed in the structures studied. A combined exciton-cyclotron resonance[21] line shows up in the reflectivity spectra in magnetic fields above 4 T. In the structure with $n_e = 9\times10^{10}\,\mathrm{cm}^{-2}$ this line shifts linearly with a slope of 0.89 meV/T, which is in very good agreement with the theoretical expectation for this value given by $\hbar\omega_c[1+m_e/(m_e+m_{hh})]$, where $\hbar\omega_c$ is the electron cyclotron energy, $m_e = 0.16m_0$, and $m_{hh} = 0.6m_0$. This combined process is based on the photogeneration of an exciton and a simultaneous excitation of a 2D electron from the zeroth to the upper Landau level. A shake-up[22] line related to X_{hh}^- has been detected in the emission spectra of a structure with $n_e = 4\times10^{10}\,\mathrm{cm}^{-2}$. It moves towards lower energies with increasing magnetic field with a slope of 0.7 meV/T, which is very close to the electron cyclotron energy of 0.725 meV/T.

To conclude, bright features in the optical spectra of ZnSe-based QW's have been identified as charged excitons. Small inhomogeneous broadening of excitonic transitions and a strong Coulombic interaction (five times stronger than that in GaAs-based QW's) allow to obtain data of high quality. Consequently ZnSe-based heterostructures lend themselves as model systems for studying exciton-electron interaction phenomena in semiconductors.

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[1] M. A. Lampert, Phys. Rev. Lett. **1**, 450 (1958).

[2] K. Kheng, R. T. Cox, Y. Merle d'Aubigne, F. Bassani, K. Saminadayar, and S. Tatarenko, Phys. Rev. Lett. **71**, 1752 (1993).

[3] G. Finkelstein and I. Bar-Joseph, Nuovo Cimento D **17**, 1239 (1995).

[4] R. T. Cox, V. Huard, K. Kheng, S. Lovisa, R. B. Miller, K. Saminadayar, A. Arnoult, J. Cibert, S. Tatarenko, and M. Potemski, Acta Phys. Pol. A **94**, 99 (1998).

[5] A. Haury, A. Arnoult, V. A. Chitta, J. Cibert, Y. Merle d'Aubigne, S. Tatarenko, and A. Wasiela, Superlattices Microstruct. **23**, 1097 (1998).

[6] A. J. Shields, J. L. Osborne, M. Y. Simmons, M. Pepper, and D. A. Ritchie, Phys. Rev. B **52**, R5523 (1995).

[7] G. Finkelstein, H. Shtrikman, and I. Bar-Joseph, Phys. Rev. B **53**, R1709 (1996).

[8] S. Glasberg, G. Finkelstein, H. Shtrikman, and I. Bar-Joseph, Phys. Rev. B **59**, R10 425 (1999).

[9] S. Ivanov, A. Toropov, S. Sorokin, T. Shubina, A. Lebedev, P. Kop'ev, Zh. Alferov, H.-J. Luagauer, G. Reuscher, M. Keim, F. Fischer, A. Waag, and G. Landwehr, Appl. Phys. Lett. **73**, 2104 (1998).

[10] K. Kheng, R. T. Cox, V. P. Kochereshko, K. Saminadayar, S. Tatarenko, F. Bassani, and A. Franciosi, Superlattices Microstruct. **15**, 253 (1994).

[11] A. V. Platonov, D. R. Yakovlev, U. Zehnder, W. Faschinger, W. Ossau, and G. Landwehr, Fiz. Tverd. Tela (Leningrad) **40**, 811 (1998) [Phys. Solid State **40**, 745 (1998)].

[12] W. Ossau, D. R. Yakovlev, U. Zehnder, G. V. Astakhov, A. V. Platonov, V. P. Kochereshko, J. Nürnberger, W. Faschinger, M. Keim, A. Waag, G. Landwehr, P. C. M. Christianen, J. C. Maan, N. A. Gippius, and S. G. Tikhodeev, Physica B **256-258**, 323 (1998).

[13] E. L. Ivchenko, A. V. Kavokin, V. P. Kochereshko, G. R. Posina, I. N. Uraltsev, D. R. Yakovlev, R. N. Bicknell-Tassius, A. Waag, and G. Landwehr, Phys. Rev. B **46**, 7713 (1992).

[14] A. Keller (private communication). Electron g factor was measured for the studied QW's by means of spin-flip Raman scattering (Ref. 15). Only weak anisotropy of the electron g factor was established $g_e^z = +1.14$ and $g_e^{x,y} = +1.17$. This value is very close to the one for bulk ZnSe of +1.15 (Ref. 16).

[15] A. A. Sirenko, T. Ruf, M. Cardona, D. R. Yakovlev, W. Ossau, A. Waag, and G. Landwehr, Phys. Rev. B **56**, 2114 (1997).

[16] B. C. Cavenett, Adv. Phys. **30**, 475 (1981).

[17] V. P. Kochereshko, D. R. Yakovlev, A. V. Platonov, W. Ossau, A. Waag, G. Landwehr, and R. T. Cox, in *Proceedings of the 23rd International Conference on the Physics of Semiconductors*, edited by M. Scheffler and R. Zimmermann (World Scientific, Singapore, 1996), p. 1943.

[18] T. Taliercio, P. Lefebvre, V. Calvo, D. Scalbert, N. Magnea, H. Mathieu, and J. Allegre, Phys. Rev. B **58**, 15 408 (1998).

[19] B. Stebe, G. Munschy, L. Stauffer, F. Dujardin, and J. Murat, Phys. Rev. B **56**, 12 454 (1997).

[20] P. Kossacki, Acta Phys. Pol. A **94**, 147 (1998).

[21] D. R. Yakovlev, V. P. Kochereshko, R. A. Suris, H. Schenk, W. Ossau, A. Waag, G. Landwehr, P. C. M. Christianen, and J. C. Maan, Phys. Rev. Lett. **79**, 3974 (1997).

[22] G. Finkelstein, H. Shtrikman, and I. Bar-Joseph, Phys. Rev. B **53**, 12 593 (1996).