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Bound Excitons in Wide-Gap II–VI and Nitride Semiconductors. Comparison of Optical Studies of Shallow Dopants in These Materials

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In this paper recent results of optical studies of bound excitons in wide-gap II–VI and nitride semiconductors are surveyed. In the first part latest results about self-compensation mechanisms will be presented. Then, the dynamical characteristics of excitonic transitions are evaluated for various impurities, dopants, and dopant concentrations, and for excitation via particular resonant excitation channels. Relaxation and conversion channels between excitonic systems are analyzed, especially in strained heteroepitaxial systems which show splitting effects of the bands from which the carriers stem. The dynamical behavior of excitons in wide-gap material gives evidence of nonradiative decay channels. Calorimetric spectroscopy at mK temperatures was used to investigate the nonradiative processes and to determine quantum efficiencies. Recent results of transient four-wave mixing experiments at bound-exciton complexes will be shown to demonstrate that shallow defects influence the dephasing in the investigated systems which gives information about the homogeneous and inhomogeneous broadening mechanisms. In the last part negatively charged excitons (trions) were observed in unintentionally donor doped $Zn_{0.90}Mg_{0.10}Se/ZnSe$ single quantum wells by magneto-luminescence experiments. The binding energy of the trion singlet ground state is about 2.7 meV.

Introduction. For growth of semiconductor devices like laser diodes and transistors, a reproducible control of doping levels for shallow acceptors and donors in the range from 10^{16} to 10^{19} cm^{-3} is the crucial prerequisite. Beside the electrical characterization, optical spectroscopy is an important probe to investigate the chemical nature of impurities, their concentration and the compensation effects involved. In wide-bandgap semiconductors like II–VI compounds and nitride based semiconductors, shallow dopands influence strongly the excitonic processes in the band edge regime. To distinguish doping effects from intrinsic properties like biexcitons or electron–hole plasmas, a detailed knowledge about the observed free and bound excitonic systems in the investigated crystal structure is mandatory. In this paper recent results obtained using photoluminescence (PL), resonant excitation spectroscopy, magneto-optics, and time-resolved analysis are surveyed.

Bound Excitons in Wide-Bandgap Material. The near-band-edge luminescence spectra of all wide-gap materials like II–VI and group-III nitride semiconductors are dominated by free- and bound-exciton-related transitions. Since shallow impurities represent the most efficient centers for the capture of free excitons and the so-formed bound

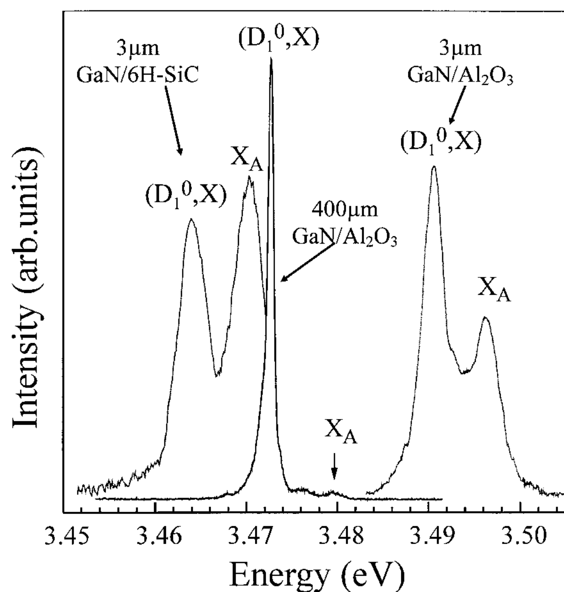

Fig. 1. The influence of biaxial strain on the luminescence of the donor-bound exciton (D_1^0,X) and the free exciton (X_A) in the low-temperature regime. The unstrained sample (400 μm) is compared to a 3 μm GaN/Al_2O_3 film (compressive strain) and to a 3 μm GaN/6H-SiC film (tensile strain)

excitons (BEs) possess a large oscillator strength of radiative recombination, spectra of not perfectly pure, as-grown material are mostly dominated by bound-exciton luminescence lines, whereas the free exciton (X_A) emission is hardly observed. The energy position and relative strength of BE luminescence lines are characteristics of the chemical nature of the impurities to which the excitons are bound and of their concentration in the material. Moreover, most of the as-grown and doped bulk samples are of n-type.

Epitaxially grown materials show changes in the excitonic luminescence spectra which exhibit some characteristics with the growth condition. First, the excitonic transitions are often split owing to the action of a layer-internal strain when growth takes place on a substrate with a lattice constant and a thermal expansion coefficient different from those of the layer material. Secondly, BE transitions serve as identification tools of impurities introduced into the layer either by diffusion from the substrate or by contamination of the material sources and the growth apparatus. An example for GaN is given in Fig. 1. Here, the luminescence in the excitonic region is compared for one 400 μm and two 3 μm layers grown on sapphire and on 6H-SiC, respectively. The 400 μm thick layer represents the strain-free case. The free (X_A) and the donor-bound (D^0,X) excitons contribute to strong radiative recombination in high-quality GaN at low temperatures. For 3 μm thin films there is an apparent blue and red shift of the excitonic luminescence, depending on whether sapphire or 6H-SiC is used as substrate material. Growth on c-plane sapphire gives rise to biaxially compressed films, while the strain is tensile for 6H-SiC. From the observation of the free-exciton transitions to different valence bands, the influence of strain on the valence band splittings can be quantified. In [1] we determined the in-plane strain $\varepsilon_{\|}$ for GaN on sapphire to 0.2% and for GaN on 6H-SiC to 0.07%.

p-Conductivity and Compensation Effects in the Wide-Bandgap Material. One of the major advances in semiconductor technology during the recent years was the realization of p-conductivity in ZnSe [2] and GaN [3], leading to optoelectronic devices in the blue spectral range like high-power light-emitting diodes and laser diodes. The major problem to be solved first was the compensation of the incorporated N and Mg accep-

tors in ZnSe and GaN, respectively, which resulted in highly resistive material even at high dopant concentrations. Today, it is clear that despite the above-mentioned success of producing p-conductive materials the compensation of acceptors is still a major problem with the group-III nitrides and semiconductors based on ZnSe. It limits the number of active acceptors to about 10^{18} cm^{-3} even if the concentration of Mg or N is much higher. Little is known of the electronic structure of compensating defects and the effects on the optical properties of GaN, while in ternary and quaternary ZnSe alloys a decrease of p-conductivity with increasing band gap was found. Up to know, no p-conductivity could be found for II–VI alloys having a band gap larger than 3.1 eV.

A way to determine the compensation degree in wide-gap materials is to investigate the transmission properties of the bound-exciton complexes. In strongly compensated semiconductors the recharging of compensated (ionized) donors and acceptors offers an efficient generation channel for free carriers and therewith for excitons. Evidence for such a recharging is contained in Fig. 2, where mono- and polychromatic absorption spectra of a ZnSe and CdS sample are depicted. The polychromatic excitation of the samples leads to a drastic increase of absorption in the bound-exciton lines. We explain this with the increased number of neutral shallow acceptors and donors recharged by photons with sufficient energy [4]. Further experiments also show that the recharging of shallow defects is achieved by intense monochromatic excitation below the band gap. For example, the 'polychromatic' transmission spectra can be observed with a tunable dye laser. In the investigated samples a degree of compensation of about 65% is determined. With known values of the net acceptor concentration of at least 8×10^{16} holes for the 0.96 μm thick sample the same amount of free electrons is generated. So we find that the amount of generated free carriers is given by the density of compensated defects. In the CdS samples we have orders of magnitude smaller amount of free carriers since these samples are not intentionally doped.

A further method to study the compensation effect in highly compensated material is to investigate the DAP PL spectra as a function of excitation densities. Typical PL spectra of compensated GaN sam-

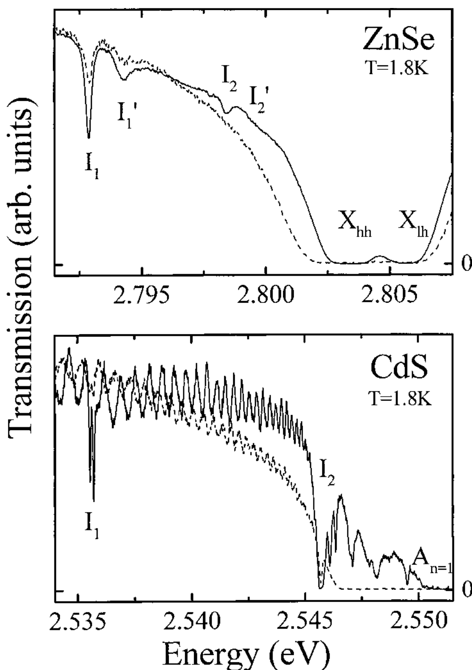

Fig. 2. Monochromatic (dashed line) and polychromatic (straight line) transmission spectra of a ZnSe epilayer (upper part) and a CdS platelet (lower part). The relative absorption depth depends linearly on the amount of neutralized bound-exciton complexes in the sample. In the monochromatic case, only the uncompensated centers contribute to the absorption

ples exhibit a characteristic change of the line shape of the DAP band. Instead of a series of LO replica of the zero-phonon line around 3.27 eV only one broad band without phonon replica is observed. Its peak is shifted strongly to lower energies. This behavior is typical for the DAP emission in strongly doped and at the same time highly compensated semiconductors and has been previously observed, e.g., in ZnSe [5] or GaAs [6]. An explanation for this behavior was discussed in detail by Shklovskii and Efros [7]. It involves strong fluctuations in the band gap at different positions in the sample caused by the electric field of a high number of compensated and, thus, ionized donors and acceptors, which are randomly distributed in the sample. At low excitation densities radiative DAP recombination takes place between the energetically lowest neutral donors and acceptors since photo-excited carriers relax quickly to these levels. A test of this model is the intensity dependence of the emission since at high excitation densities the concentration of photo-excited carriers is high enough to neutralize most donors and acceptors and the band fluctuations should vanish. Therefore, at the highest densities the well-known structured DAP emission line shape as seen in samples with low compensation should be observed. This was indeed the case for compensated ZnSe : N [5].

To test this model for GaN : Mg we studied the intensity dependence of the PL of the highly resistive sample grown with a Cp_2Mg/TEGa ratio of 0.3%. It is shown in Figs. 3a and 3b for two different excitation conditions. In Fig. 3a we used a focused continuous-

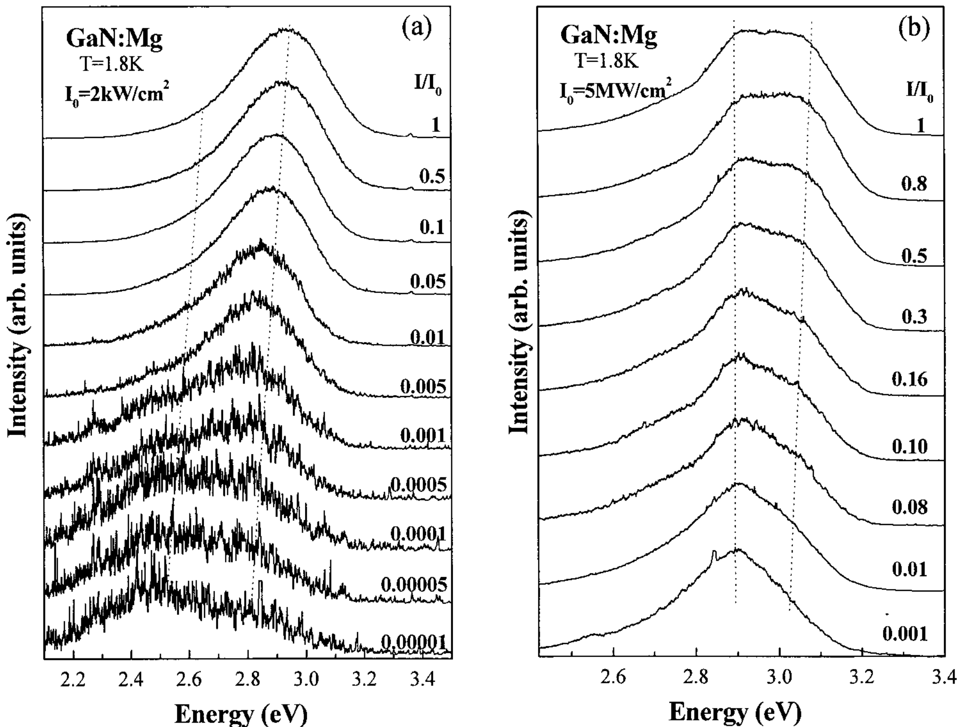

Fig. 3. Energy dependence of the normalized PL of a p-type GaN epilayer doped with 0.3 Mg; measured with a) a cw-HeCd laser at up to 2 kW/cm^2 and b) the third harmonic of a pulsed Nd : YAG laser with pulse intensities up to 5 MW/cm^2

wave (cw) HeCd laser with a maximum density of 2 kW/cm^2, and in Fig. 3b the focus of a pulsed Nd:YAG laser system to obtain even higher excitation densities. Starting from lowest excitation intensities in Fig. 3a we observed two broad emission bands around 2.45 eV and 2.8 eV. Assuming a Gaussian line shape for both luminescences we fitted the spectra of Fig. 3a and obtained very good agreement with the measurements. Raising the excitation density the high-energy band exhibits a growth in integrated intensity with a slope of one, exactly the same as that observed for compensated ZnSe:N [5]. Also the observed logarithmic shift of the peak energy to higher energies with increasing excitation density is in agreement with the behavior of other strongly doped and compensated semiconductors. This shift is the same for both emission bands.

The total blue shift of the high-energy band between 20 mW/cm^2 and 2 kW/cm^2 is about 153 meV. Using the pulsed laser source the excitation density per pulse can be increased up to 5 MW/cm^2. The result of this experiment for the compensated 0.3% sample is shown in Fig. 3b. We find that the blue shift of the high-energy band saturates around 2.91 eV. On the high-energy shoulder of this band a new emission line grows, again shifting to higher energies with increasing excitation intensity. At the highest density of 5 MW/cm^2 it is found at 3.06 eV, 210 meV below the well-known DAP ZPL in weakly compensated GaN. Summarizing the results, in GaN a transition from a structured DAP band to a broad emission band shifted to lower energies is observed with increasing concentration of Mg acceptors. This is in agreement with observations on other compensated semiconductors. The compensation mechanism seems to be correlated directly to the increased incorporation of Mg into GaN. For a highly compensated sample studied in intensity-dependent measurements the expected observation of a structured DAP band at highest excitation densities, following the model of Shklovskii and Efros cannot be accomplished up to 5 MW/cm^2. Instead of a continuous shift of the emission peak to higher energies a saturation of the blue shift accompanied by the growth of a new emission is observed.

Our intensity-dependent PL measurements on highly compensated p-doped GaN:Mg show that different deep donor levels related to the Mg-doping are responsible for the compensation of the shallow acceptor. Three deep donors at 240 ± 30 meV, 350 ± 30 meV, and 850 ± 30 meV from the conduction band were found. They are subsequently neutralized with increasing excitation density giving rise to deep unstructured donor–acceptor pair emissions. Thus, deep defects and not band fluctuations are the dominant mechanism for the observation of deep DAP emissions in GaN:Mg.

Radiative and Nonradiative Decay of Bound Excitons in Wide-Bandgap Semiconductors. It is well known that the temporal behavior of bound-exciton recombination in wide-bandgap materials is ideally suited for impurity characterization, analysis of excitation channels and study of the influence of external parameters, e.g. strain. In a review paper [8] experimental data on rise and decay times of free and bound exciton transitions in II–VI bulk and epitaxial grown material are summarized. Often, a strong decrease of the free exciton lifetimes down to a few ten ps in connection with an increase of the concentration of the dopant could be seen, indicating that nonradiative decay channels are involved. Typical lifetimes of excitons weakly bound to neutral donors or acceptors are between 40 ps to 1 ns in these materials which are independent of doping concentrations. In particular, the large amount of bound excitons in the ZnO spectrum [9] can be compared in detail with model calculations of [10] revealing a reasonable

agreement for radiative decay. Here, time-resolved investigations enable us to determine or to check effective mass or the oscillator strength of the free exciton. In Fig. 4 transients of the radiative decay of acceptor-bound excitons in ZnSe and CdS are compared. The energy relaxation times amount some hundred ps and will be discussed in the next section.

To quantify the contribution of nonradiative processes to the recombination mechanism near the band gap we employed calorimetric spectroscopy. This technique enables us to measure directly the temperature increase of the photo-excited sample as a function of excitation energy. Fig. 5 gives sets of simultaneously recorded high-resolution calorimetric absorption (P_{CAS}), transmission (P_{CTS}), and reflection (P_{CRS}) spectra taken of a thin bulk CdS sample in comparison to the exciting light (P_{IN}). The spectra exhibit the resonances of the bound excitons I_1, I_2, I_3, and I_{1B}. Additionally, the free excitons $X_{An=1}$, $X_{Bn=1}$, and their excited states $X_{An=2}$ and $X_{Bn=2}$ can be detected. The P_{CRS} spectrum shows at 2.53 eV a reflection of nearly 40 % since multiple reflection contributes to the signal. With these calorimetric data we are able to calculate macroscopic quantum efficiencies (QEs) of the different resonances. The QE of the bound excitons is 25% for I_1 and 21% for I_2. In comparison to these values the QE of the free excitons is lower: 20% and 18% for $X_{An=1}$ and $X_{Bn=1}$, respectively. As a result, most of the relaxation leads to a heating of the sample whereas only a fourth of the exciting light is converted into luminescence which can leave the crystal.

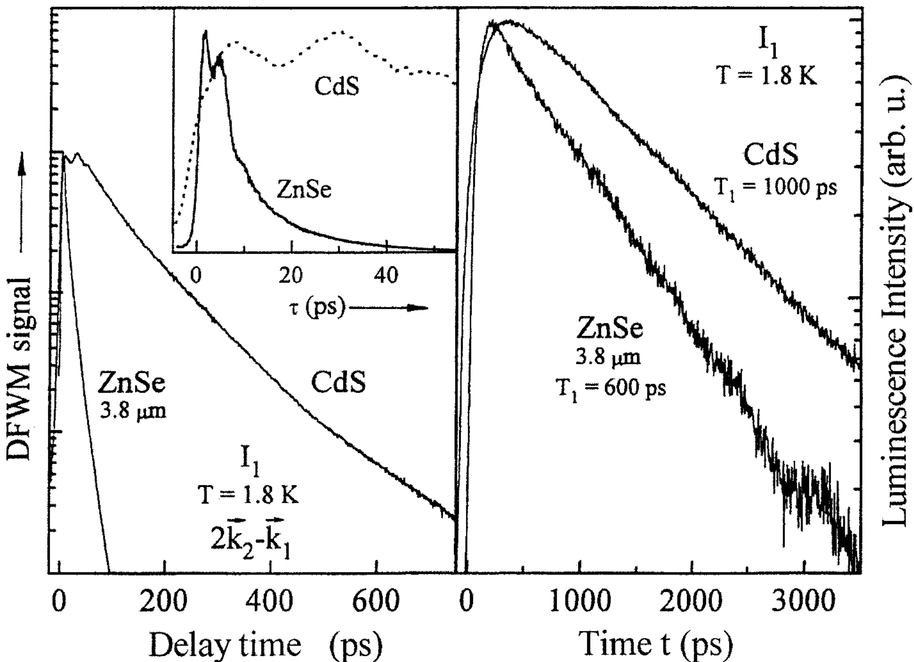

Fig. 4. DFWM (left part) and luminescence transients (right part) of the A^0,X resonance in CdS and ZnSe. The inset shows DFWM transients on a linear scale clearly revealing a beat structure for short delay times. Although the energy relaxation times are nearly equal, the dephasing times observed in ZnSe are decreased significantly caused by stronger dephasing processes induced by the higher amount of shallow defect levels

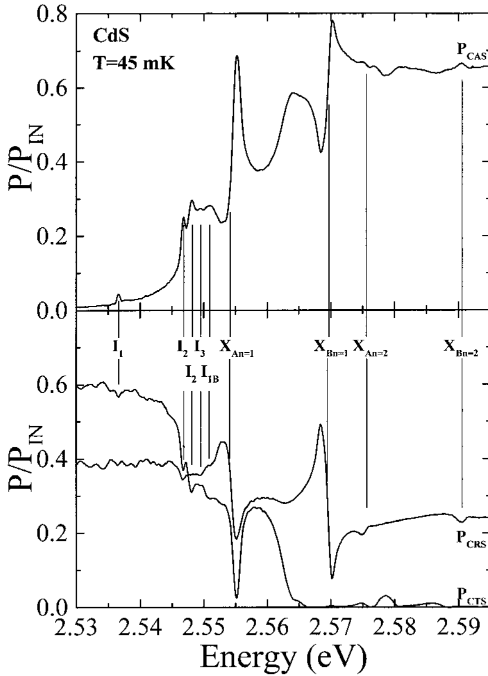

Fig. 5. Calorimetric absorption spectroscopy of a CdS crystal. In the upper part the heating of the sample (calorimetric absorption P_{CAS}) is depicted. The lower part contains the calorimetric transmission (P_{CTS}) and the reflection of the crystal (P_{CRS}). All spectra are shown in relation to the exciting light (P_{IN})

Dephasing of Bound-Exciton States. For a strongly localized system as the acceptor-bound exciton in ZnSe or CdS one expects long dephasing times (T_2) governed by the energy-relaxation process (T_1), giving $T_2 = 2T_1$. For CdS and ZnSe we determine the energy-relaxation time T_1 of the I_1 transition with time-resolved luminescence to be 1000 ps and 600 ps, respectively (right part of Fig. 4). For the investigated samples degenerated four-wave-mixing experiments (DFWM) in the self-diffraction geometry yield (left part of Fig. 4) a dephasing time T_2 of 800 ps in CdS and 70 ps in ZnSe for the neutral-acceptor-bound exciton complex. These values have been extracted from transients recorded at low excitation densities and at low temperatures using the fact that transition is inhomogeneously broadened [11]. Interestingly, the dephasing times in the ZnSe samples are drastically decreased compared to CdS, although the energy relaxation times are nearly equal.

To get additional information of the dephasing mechanisms, the DFWM signal as a function of temperature and excitation densities was measured. From the temperature dependence we conclude that at $T = 2$ K phonons do not influence the dephasing of the neutral-acceptor-bound exciton complex [11]. The dependence of the DFWM signal on the excitation density shows a nonexponential decay of the transients for a delay time of about 200 ps, independent of the excitation density. A nonexponential decay of the DFWM transients indicates interactions with a time-dependent bath. This was modeled in Ref. [12]. From the fit parameter we obtain a dephasing time of about 800 ps, the bath density N remains nearly constant and the lifetime of the bath increases with increasing excitation density from 160 ps to 500 ps. As phonons are excluded, we propose free excitons to form the time-dependent bath because these are mobile excitations with an appropriate lifetime.

Trions in Quantum Wells. In doped quantum well systems like GaAs/AlGaAs [13] or CdTe/CdZnTe [14] a significant amount of doping-induced excess carriers accumulated in the wells results in a formation of negative or positive excitons (trions). Since the trion binding energy is small, e.g. 2 to 4 meV in CdTe/CdZnTe, the stability of trions

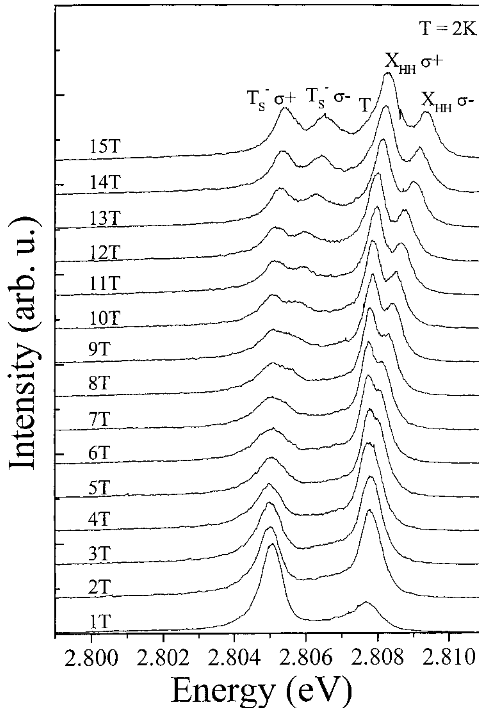

Fig. 6. PL spectra of a ZnSe/ZnMgSe single quantum well (25 nm) under different magnetic fields in Voigt configuration (**k** ⊥ **B**). Under higher magnetic fields starting at 8 T, on the low-energy tail of the heavy-hole exciton (X_{hh} σ^+) two trion triplet states were separated

depends sensitively on the excitonic band structure of the investigated material system.

As an example, here we present PL investigations of trions as a function of magnetic field in ZnSe/ZnMgSe quantum wells. The samples we used were grown by molecular beam epitaxy (MBE) with a well width between 10 nm and 25 nm and various donor background concentrations in the barriers. The Mg content was 10%.

In Fig. 6 Zeeman investigations in Voigt configuration (**k** ⊥ **B**) are depicted. Under high magnetic fields a separation between the twofold spin degenerated singlet ground state of the trion can be seen (T_S^- σ^+ and T_S^- σ^+) in accordance to the selection rules applied to trions. Additionally, from the low-energy tail of the heavy-hole exciton (X_{hh} σ^+) under higher magnetic fields starting at 8 T, two additional recombinations (T) were separated. We attribute them to the trion triplet states with the lowest energy regarding to the sixfold degeneration of this excited state. Magnetic field dependent PL investigations with different orientation angles between the field and the sample surface enable us to construct the term scheme [15]. To exclude that biexcitons or donor-bound excitons contribute to the observed luminescence structures, additional polarization dependent investigations like four-wave-mixing experiments or reflectivity measurements have to be performed.

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