1. Introduction

Epitaxial quantum dots (QDs) are renowned for their diversity—in a single sample one can find QDs with different values of emission energy, anisotropy-induced exchange splitting, effective Landé factor, diamagnetic shift, and other parameters. It can be an advantage, if a single QD with particular properties (e.g. zero anisotropy splitting [1, 2]) is required. On the other hand, such a diversity is an obstacle on the way to determine the typical behavior of QDs in a given material system.

Precise determination of the typical QD parameters requires averaging over many individual dots. In case of some characteristics, such as emission energy or g-factor, it is possible to simply measure the response of the whole QD ensemble [3–6], e.g. in photoluminescence (PL) or time-resolved Faraday rotation experiments, respectively. However, more detailed characteristics such as anisotropic fine-structure splitting (FSS) can be studied directly only on a single-dot level and thus a significant number of individual dots need to be analyzed in order to draw robust conclusions about the average value.

In this work we present results of systematic comparison between the two popular II–VI self-assembled QD systems: CdTe/ZnTe and CdSe/ZnSe. We particularly focus on differences between excitons of various charge states: their binding energy X−XX, their fine-structure splitting $\delta = 0.14$ meV ($\delta = 0.47$ meV); g-factor $g = 2.12$ ($g = 1.71$); diamagnetic shift $\gamma = 2.5$ meV T$^{-2}$ ($\gamma = 1.3$ meV T$^{-2}$). We find also statistically significant correlations between various parameters describing internal structure of excitonic complexes.

Keywords: CdTe/ZnTe, CdSe/ZnSe, quantum dot, spectroscopy, Landé factor $g$, diamagnetic shift, fine-structure splitting

(Some figures may appear in colour only in the online journal)
energy, \( g \)-factor and diamagnetic shift. These quantities have been already measured for single quantum dots \([7–18]\), but have not been analyzed in terms of variation across the QD population.

2. Samples and experimental setup

We studied 3 structures with CdSe QDs in ZnSe barriers and 4 structures with CdTe QDs in ZnTe barriers. Samples were fabricated in three different laboratories (affiliations 1–3). The growth of the structures was performed by molecular beam epitaxy (MBE) on GaAs substrates. In most cases the reorganization of the QDs was induced by a well-established amorphous Te or Se desorption method \([19–21]\) for which the growth temperature was varied just after deposition of the QD formation layer. For the two selenide samples the cap layer was deposited directly on the QD layer without changing the substrate temperature. In order to reduce QD density in selenide samples we applied additional low level delta-doping with transition metal ions \([22–24]\). However, in this work we include only results obtained for individual QD, which do not contain magnetic ions inside.

The studied samples were placed inside a magneto-optical bath cryostat with magnetic field of up to 10 T. The measurements were performed at the temperature of about 1.5 K using a reflective type microscope, which focuses the laser beam to a 0.5 \( \mu \)m diameter spot. This allowed us to study optical properties of well-resolved emission lines of single QDs in high magnetic fields with a polarization resolution. Complementary magneto-optical studies were performed in Grenoble High Magnetic Field Laboratory, where a helium-bath cryostat (4.2 K) with a sample was placed inside a 20 MW resistive magnet producing magnetic field of up to 28 T.

3. Results

In order to present statistically significant data we have investigated over 160 individual QDs. For each analyzed QD we studied emission lines originating from the recombination of the neutral exciton \( X \), the biexciton \( XX \), and the charged excitons \( \ (X^+ \), \( X^- \)). The spectra of telluride QDs typically feature also additional emission lines related to higher excitonic complexes, e.g. doubly negatively charged exciton \( (X^2^-) \) and negatively charged biexciton \( (XX^-) \). However, for the sake of consistency, the following discussion is limited to the set of four basic transitions observed in both QD systems. Identification of such transitions has been already discussed in detail elsewhere \([8, 11, 25–27]\). Typically it includes the analysis of linear polarization of emission and the dependence of the PL intensity on the excitation power. Based on the PL spectra measured in magnetic field of 0–10 T we extracted parameters describing each of the studied excitonic transitions: their relative emission energies, anisotropy-induced exchange splittings, effective Landé \( g \)-factors, and diamagnetic shift coefficients \( \gamma \).

3.1. Relative emission energy of \( X, XX, X^+, \) and \( X^- \)

The energy of the emission lines related to particular QD strongly depends, e.g. on the growth procedure and the QD size \([21]\), but in this work we focus rather on the structure of a PL spectrum of a single QD. Figures 1(a) and (b) present PL spectra of a single CdSe/ZnSe and CdTe/ZnTe QDs. Solid lines mark the linear fits \( (y = ax) \) with proportionality constants equal to \( a_{\text{CdSe}} = 0.64, a_{\text{CdTe}} = 0.78, a_{\text{CdSe}} = 0.45, a_{\text{CdTe}} = 0.95 \) (compare with \([26, 28]\)). Dashed line corresponding to \( y = x \) is drawn for the reference.
with [26, 28] we find that for telluride QDs the distances between the emission lines vary almost proportionally to each other (figure 1(c)). Consequently, the emission pattern stays roughly the same, except for some variation of the horizontal scale. Such an effect significantly simplifies identification of the PL lines originating from a single CdTe/ZnTe QD in the experiment. As shown in figure 1(c), the situation in the selenium system is different. Distances between the X+, X’ and X lines in case of the selenium QDs cannot be considered proportional to the X–XX distance. Although there exists some positive correlation between the X–X’+, X–X’– distances and the X–XX distance (Pearson’s correlation coefficients $r_X = 0.58$ and $r_{X’} = 0.66$, compared to $r_X = 0.87$ and $r_{X’} = 0.87$ found for the tellurides), their relationship does not correspond to a simple proportionality (see figure 1(c)). We note that while all studied CdTe QDs exhibited the same sequence of excitonic transitions in the PL spectrum, for the selenide QDs the negatively charged exciton line can be situated either on higher or on lower energetic side of the neutral biexciton line.

Another important difference between the two material systems is the average value of the relative X–XX transition energy distance. In the case of telluride QDs such an average energy distance is equal to about 1.20 meV, while for the selenide QDs the obtained average value is about twice as high and yields 23.9 meV.

3.2. Anisotropic exchange splitting of X and XX

By means of the PL measurements performed with a polarization resolution of detection we analyzed the fine-structure of the X and XX states for CdTe and CdSe QDs (figure 2). In the case of both excitonic complexes the zero-field emission contains two lines split by the energy related to the anisotropic part of the exchange interaction between the electron and the heavy hole [10, 18]. Such emission lines can be seen separately in two perpendicular linear polarizations of the detection. As expected, for each QD we observed the same value of anisotropy splitting of X and XX, but opposite ordering of the fine-structure-split components for both complexes. This is due to the fact that X is the final state of the XX transition. In the experiment, for each studied dot we collected the PL spectra as a function of linear polarization angle of detection. Such a measurement provides information not only about the value of the fine-structure splitting ($\delta_0$) but also about the in-plane anisotropy axis of each QD [30]. In contrast to III–V QDs [32], we do not observe any notable correlation between the in-plane anisotropy parameters (splitting and direction) and the crystallographic axes, the transition energy and the biexciton relative energy, which is consistent with the previous reports on II–VI QDs [26, 31]. For the telluride QDs the average value of the fine-structure splitting $\delta_1$ is about 0.14 meV, whereas for the selenide QDs we found a few times higher average value of $\delta_1 = 0.47$ meV.

3.3. Zeeman effect and diamagnetic shift

The energy spectrum of the QD can be manipulated by external magnetic field. Two main effects occurring upon application of the magnetic field are a linear splitting of the states depending on the spin projection (Zeeman effect) [10, 11, 13] and a quadratic energy shift due to a finite spatial extension of the exciton wave function (diamagnetic shift) [7, 13]. The strength of these effects is parametrized with the excitonic $g$-factor and the diamagnetic field coefficient $\gamma$.

In our experiments we studied these parameters in the Faraday geometry with the magnetic field applied along the growth axis of the QDs. As expected, the transitions of all considered excitonic complexes exhibit a common field-induced splitting pattern comprising of two lines separated by the energy of $\sqrt{\Delta^2 + (g\mu_B B)^2}$, where $g$ is the $g$-factor, while $\Delta$ corresponds to the zero-field splitting (equal to $\delta_1$ for the neutral complexes and 0 in case of the trions). In order to take into account the change of the mean emission energy (originating from the diamagnetic shift), we fitted both Zeeman branches of a given transitions with a quadratic formulas of the form $E(B) = E_0 \pm \frac{1}{2} \sqrt{\Delta^2 + (g\mu_B B)^2} + \gamma B^2$, where $+$ (−) sign corresponds to the higher (lower) energy line.

The results of the fitting are presented in figure 3. The average $g$-factor of the CdTe QDs ($g = 2.12$) was found to be slightly larger than the average $g$-factor of the CdSe QDs ($g = 1.71$). We stress that both $g$-factors are positive, as in both QD systems the Zeeman-split emission lines exhibit exactly the same polarization behavior, with the high (low) energy component being $\sigma^+$ ($\sigma^-$) polarized. More significant differences were obtained by studying the diamagnetic shift, which was found to be approximately two times higher for the telluride QDs (2.5 $\mu$eV T$^{-2}$) compared to the selenide ones (1.3 $\mu$eV T$^{-2}$), as shown in figures 3(c), (f). These values can be expressed using a more comprehensive quantity of the spatial extension of the excitonic wave function according to a relation
where \( m \) is the in-plane reduced mass of the exciton. One should note that this expression is strictly valid only for the systems with translational symmetry in the plane perpendicular to the magnetic field (i.e. in bulk or quantum wells) [7]. By applying this formula also to the case of QDs we obtained the values of the spatial extension of the excitonic wave function in normal configuration for CdSe and CdTe QDs as \( r = 2.4 \) nm and \( 3.1 \) nm, respectively. Such values stay in a good agreement with the material trends. More specifically, dielectric constant is smaller for the selenides [33], which leads to a stronger electron-hole interaction. As a consequence, the CdSe QDs exhibit stronger exciton binding and smaller radius of the excitonic wave function. The obtained values can be also compared with the bulk exciton radii, which yield 5.6 nm for CdSe and 7.5 nm for CdTe [34]. In each system the confinement in the QD potential reduces the extension of the exciton wavefunction, yet only up to about 60%.

The most surprising findings are obtained from the correlations between the effective Landé g-factors determined for different excitonic complexes. Since each of the studied lines is related to the recombination of an s-shell hole with an s-shell electron, all these transitions for a given QD are expected to exhibit the same excitonic g-factor. Nevertheless, Léger et al [15] reported about a CdTe QD with different values of g-factors for various excitonic complexes. Our measurements corroborate this claim and demonstrate the existence of a systematic deviation between the g-factors of X, X⁺, and X⁻ transitions in the whole population of the QDs. Such a systematic difference was found in both systems, but with opposite sign, as seen in figure 4.

In the case of CdTe QDs we observed with perfect regularity that the g-factor of the neutral exciton is greater than the g-factor of the X⁻ and smaller than the g-factor of the X⁺. The average difference between the g-factor values corresponding to X⁺ and X was equal to 0.34, while the difference between the g-factor of X⁻ and X was about three times smaller (0.11). For the selenide QDs we observed opposite sign of this effect: greater values of the g-factors for X⁻ states and smaller for X⁺ states in comparison to X Landé factor. However, due to significantly lower mean values of the g-factor differences and fluctuations of the g-factor distribution we found a few exceptions from such an ordering. With respect to the X g-factor, Landé factor of X⁻ state was on average larger by 0.03, while the g-factor of X⁺ state was smaller by about 0.04. We interpret the observed differences between the g-factor values for various excitonic complexes as resulting from significant modification of the carrier wave function imposed by the presence of the other carriers in the dot [15].

\[
\gamma = \frac{e^2}{8m}(r^2),
\]

\((1)\)
We note that for both QDs systems the Landé factors of X and XX were equal for all dots within our experimental uncertainty. Such a relation is expected, since the singlet nature of the bie exciton state implies that the Zeeman effect of the XX transition originates solely from the final state, i.e. the neutral exciton state. Average differences of the g-factors of X and XX states were equal 0.006 and 0.007 for telluride and selenide QDs, respectively, which is indeed much smaller than differences between the charged excitons g-factors discussed earlier.

In analogy to the study of the Landé factors, we also investigated correlations between diamagnetic shift constants for various excitonic complexes. For both QDs systems we do not observe any systematic differences, except that for selenide QDs the diamagnetic shift of the X tended to be slightly larger than for the other complexes. However, in the case of CdTe QDs we obtained similar values of the diamagnetic shifts coefficients for various excitons in a given dot.

4. Summary

By means of magneto-optical techniques we have studied and compared the two systems of self-organized QDs: CdTe/ZnTe and CdSe/ZnSe QDs. We investigated over 160 randomly selected individual QDs. To reduce the influence of the effects related to the growth technique and specific sample, we examined 7 structures fabricated in 3 laboratories. Based on such statistical approach we determined the key parameters describing magneto-optical properties of the excitonic complexes in CdTe/ZnTe and CdSe/ZnSe QDs. The average values of the characteristic parameters describing the studied QDs are summarized in table 1.

Typical spectra of individual CdTe QD contain several emission lines that form a characteristic pattern. For most of the studied CdTe dots the energy distances between the emission lines related to various charged states vary proportionally to the energy distance of X and XX. In the case of selenide QDs we observed much weaker correlation of the relative energy positions of the emission lines. Furthermore, the sequence of the emission lines is not conserved for all dots, i.e. the energy of X− emission line can be either higher and lower than the energy of XX line. Analysis of the magnetic field dependence of the emission spectra revealed an unexpected effect of the systematic difference between the g-factors of various excitonic complexes, especially for the CdTe system.

The comparison between the parameters determined for CdTe and CdSe QDs is consistent with the general material trends. In particular, the smaller dielectric constant of selenides [33] leads to a stronger Coulomb interaction between the carriers, which is reflected by the higher bulk exciton binding energy [35–39]. Similarly, the selenide QDs exhibit larger energetic distance between the exciton and the biexciton emission lines, larger anisotropic part of the electron-hole exchange interaction and tighter binding of the carriers in the excitonic complexes evidenced by a smaller value of the diamagnetic shift coefficient.

Acknowledgments

This work was partially supported by the Polish National Science Centre under decisions DEC-2012/05/N/ST3/03209, DEC-2013/09/B/ST3/02603, DEC-2011/02/A/ST3/00131, and by Polish Ministry of Science and Higher Education in years 2012–2017 as research grants ‘Diamantowy Grant’ and Juventus Plus (No. IP2014 034573). The two of us (JK and TS) were supported by the Foundation for Polish Science through the START programme. The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007–2013) under grant agreement No. 316244. Project was carried out with the use of CePT, CeZaMat, and NLTK infrastructures financed by the European Union—the European Regional Development Fund within the Operational Programme ‘Innovative economy’.

References

[1] Young R J, Stevenson R M, Shields A J, Atkinson P, Cooper K, Ritchie D A, Groom K M, Tartakovskii A I and Skolnick M S 2005 Inversion of exciton level splitting in quantum dots Phys. Rev. B 72 113105
[2] Stevenson R M, Young R J, Atkinson P, Cooper K, Ritchie D A and Shields A J 2006 A semiconductor source of triggered entangled photon pairs Nature 439 179
[3] Zhang S K, Myint T, Wang W B, Das B B, Perez-Paz N, Lu H, Tamargo M C, Shen A and Alfano R R 2010 Optical study of strongly coupled CdSe quantum dots J. Vac. Sci. Technol. B 28 C3D17
[4] Sypercek M, Yakovlev D R, Yugova I A, Misiewicz J, Sedova I V, Sorokin S V, Toropov A A, Ivanov S V and Bayer M 2011 Long-lived electron spin coherence in CdSe/Zn(S,Se) self-assembled quantum dots Phys. Rev. B 84 085304
[5] Reshina I I, Ivanov S V and Toropov A A 2012 Magneto-optical studies of ensembles of semimagnetic self-organized Cd(Mn)Se/Zn(Mn)Se quantum dots Phys. Rev. B 86 155302
[6] Man M T and Lee H S 2015 Discrete states and carrier-phonon scattering in quantum dot population dynamics Sci. Rep. 5 8267
[7] Walck S N and Reineneck T L 1998 Exciton diamagnetic shift in semiconductor nanostructures Phys. Rev. B 57 9088
[8] Kulakovskii V D, Bacher G, Weigand R, Kümme1l T, Forchel A, Borovitskaya E, Leonard K and Hommel D 1999 Fine structure of biexciton emission in symmetric and asymmetric CdSe/ZnSe single quantum dots Phys. Rev. Lett. 82 1780

Table 1. Average values of the parameters describing CdTe and CdSe QDs.

|          | CdSe/ZnSe QDs | CdTe/ZnTe QDs |
|----------|---------------|---------------|
| $E_X - E_{XX}$ (meV) | 23.9 ± 2.6 | 12.0 ± 1.2 |
| $g_X$ (meV) | 0.47 ± 0.21 | 0.14 ± 0.08 |
| $g_{XX}$ (number) | 1.71 ± 0.21 | 2.12 ± 0.30 |
| $g_{XX} - g_X$ (number) | −0.04 ± 0.07 | 0.34 ± 0.11 |
| $g_{XX} - g_X$ (number) | 0.03 ± 0.08 | −0.11 ± 0.07 |
| $\gamma_X$ (u.eV T$^{-2}$) | 1.3 ± 0.5 | 2.5 ± 1.2 |

Note: The symbols are introduced and explained in the text. Uncertainties were calculated as a standard deviation of the determined parameters.
[9] Hundt A, Flissikowski T, Lowisch M, Rabe M and Henneberger F 2001 Excitation spectrum, relaxation and coherence of single assembles CdSe quantum dots Phys. Status Solidi b 224 159

[10] Bayer M et al 2002 Fine structure of neutral and charged excitons in self-assembled In(Ga)As/(Al)GaAs quantum dots Phys. Rev. B 65 195315

[11] Besombes L, Kheng K, Marsal L and Mariette H 2002 Few-particle effects in single CdTe quantum dots Phys. Rev. B 65 121314

[12] Finley J J, Mowbray D J, Skolnick M S, Ashmore A D, Baker C, Monte A F G and Hopkinson M 2002 Fine structure of charged and neutral excitons in InAs-Al_{0.5}Ga_{0.5}As quantum dots Phys. Rev. B 66 153316

[13] Schulhauser C, Høgele A, Warburton R J, Govorov A O, Schoenfeld W, Garcia J M, Petroff P M and Karr K 2003 Magnetic properties of charged excitons in self-assembled quantum dots Phys. Status Solidi b 238 293

[14] Akimov I A, Kavokin K V, Hundt A and Henneberger F 2005 Electron-hole exchange interaction in a negatively charged quantum dot Phys. Rev. B 71 075326

[15] Léger Y, Besombes L, Maingault L and Mariette H 2007 Valence-band mixing in neutral, charged, and Mn-doped self-assembled quantum dots Phys. Rev. B 76 045331

[16] Oberli D Y, Byszewski M, Chalupar B, Pelucchi E, Rudra A and Kapon E 2009 Coulomb correlations of charged excitons in semiconductor quantum dots Phys. Rev. B 80 165312

[17] Hewaparakrama K P, Mackowski S, Jackson H E, Smith L M, Heiss W and Karczewski G 2008 Tuning spin properties of excitons in single CdTe quantum dots by annealing Nanotechnology 19 125706

[18] Puls J, Rabe M, Wünsche H-J and Henneberger F 1999 Magneto-optical study of the exciton fine structure in self-assembled CdSe quantum dots Phys. Rev. B 60 R16303

[19] Tingjöf D, Gilles B, Moehl S, Kheng K and Mariette H 2003 II–VI quantum dot formation induced by surface energy change of a strained layer Appl. Phys. Lett. 82 4340

[20] Wojnar P, Bougerol C, Bellet-Amalric E, Besombes L, Mariette H and Boukari H 2011 Towards vertical coupling of CdTe/ZnTe quantum dots formed by a high temperature tellurium induced process J. Cryst. Growth 335 28

[21] Kobak J, Rousset J-G, Rudniewski R, Janik E, Slupinski T, Kossacki P, Golnik A and Pacuski W 2013 Ultra low density of CdTe quantum dots grown by MBE J. Cryst. Growth 378 274

[22] Kobak J, Smoleński T, Goryca M, Papaj M, Gietka K, Bogucki A, Koperski M, Rousset J-G, Sufczynski J, Janik E, Nawrocki M, Golnik A, Kossacki P and Pacuski W 2014 Designing quantum dots for solotronics Nat. Commun. 5 3191

[23] Smoleński T, Pacuski W, Goryca M, Nawrocki M, Golnik A and Kossacki P 2015 Optical spin orientation of an individual Mn^{2+} ion in a CdSe/ZnSe quantum dot Phys. Rev. B 91 045306

[24] Smoleński T, Kazimierzczuk T, Kobak J, Goryca M, Golnik A, Kossacki P and Pacuski W 2016 Magnetic ground state of an individual Fe^{2+} ion in strained semiconductor nanostructure Nat. Commun. 7 10484

[25] Sufczyński J et al 2006 Excitation mechanisms of individual CdTe/ZnTe quantum dots studied by photon correlation spectroscopy Phys. Rev. B 74 085319

[26] Kazimierzczuk T, Smoleński T, Goryca M, Klopotsowski L, Wojnar P, Fröck K, Golnik A, Nawrocki M, Gaj J A and Kossacki P 2011 Magnetophotoluminescence study of intershell exchange interaction in CdTe/ZnTe quantum dots Phys. Rev. B 84 165319

[27] Kazimierzczuk T, Smoleński T, Kobak J, Goryca M, Pacuski W, Golnik A, Fröck K, Klopotsowski L, Wojnar P and Kossacki P 2013 Optical study of electron–electron exchange interaction in CdTe/ZnTe quantum dots Phys. Rev. B 87 195302

[28] Kobak J, Pacuski W, Jakubczyk T, Kazimierzczuk T, Golnik A, Frank K, Rosenauer A, Krause C, Holmdel M and Gaj J A 2011 Optical properties of CdTe QDs formed using Zn induced reorganization Acta Phys. Pol. A 119 627

[29] Zielinski M et al 2015 Excitonic complexes in natural InAs/GaAs quantum dots Phys. Rev. B 91 085303

[30] Bogucki A, Smoleński T, Goryca M, Kazimierzczuk T, Kobak J, Pacuski W, Wojnar P and Kossacki P 2016 Anisotropy of in-plane hole g-factor in CdTe/ZnTe quantum dots (arXiv:1604.02591)

[31] Kudelski A, Golnik A, Gaj J, Mackowski S, Karczewski G and Kossut J 2001 Zeeman effect and optical anisotropy in microluminescence of self-assembled CdTe/ZnTe quantum dot systems Proc. of the 25th Int. Conf. on Physics of Semiconductors (Springer, Osaka, 2000) pp 1249–50

[32] Molas M, Golasa K, Piętka B, Potemski M and Babioński A 2012 Fine structure of neutral excitons in single GaAlAs quantum dots Acta Phys. Pol. A 122 988

[33] Strzałkowski I, Joshi S and Crowell C R 1976 Dielectric constant and its temperature dependence for GaAs, CdTe, and ZnSe Appl. Phys. Lett. 28 350

[34] Landolt-Boernstein 1998 Group III Condensed Matter vol 41C (Berlin: Springer)

[35] Voigt J, Spiegelberg F and Senoner M 1979 Band parameters of CdS and CdSe single crystals determined from optical exciton spectra Phys. Status Solidi b 91 189

[36] Nawrocki M and Twardowski A 1980 Oscillatory Magnetooabsorption in CdTe Phys. Status Solidi b 97 K61

[37] Wagner H, Lankes S, Wolf K, Wez M, Reisinger T, Naumov A, Kuhn W, Stanzl H and Gebhardt W 1993 Resonant photoluminescence measurements in As- and P-doped ZnTe epilayers Physica B 185 169

[38] Aliév G, Koschuch O and Seisyan R 1994 High-temperature effectiveness limit of exciton-polariton processes in cadmium and zinc telluride crystals Phys. Solid State 36 203

[39] Wörz M, Griebel E, Reisinger T, Fliert R, Haserer B, Semmler T, Frey T and Gebhardt W 1997 Gap energies, exciton binding energies and band offsets in ternary ZnMgSe compounds and ZnSe/ZnMgSe heterostructures Phys. Status Solidi b 202 805