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Self-report

Contents

1	Education and degrees	2
2	Information on previous employment	2
3	Bibliometric data	3
4	Scientific achievement being the basis of the habilitation procedure	4
4.1	Introduction — from epitaxy to nanostructures	5
4.2	Properties and potential applications of quantum dots	7
4.3	Motivation — cadmium telluride quantum dots	11
4.4	Manipulation of exciton state in a single cadmium telluride quantum dot	13
5	Description of other scientific achievements	23
5.1	Research done before obtaining the PhD title	23
5.2	Research done after obtaining the Ph.D. title: works not related to the topic of the thesis	24
5.3	Research done after obtaining the Ph.D. title: works related to the topic of the thesis	30
5.4	Participation in research projects	31
5.5	Conference talks	31
5.6	Collaborations with international and Polish institutions	33
5.7	Research visits	33
5.8	Awards	34
6	Other activities	34
6.1	Teaching	34
6.2	Outreach	35
6.3	Organizational activities	35
6.4	Development of the workplace	35

1 Education and degrees

- Ph. D. *cum laude*: University of Warsaw, Faculty of Physics, March 10th, 2003.
Title of thesis: *Magneto-optical Study of Exciton Tunneling in Asymmetric Double Quantum Well Structures*
Advisor: prof. dr hab. Michał Nawrocki
- Stopień magistra fizyki: University of Warsaw, Faculty of Physics, October 30th 1997.
Title of thesis: *Wpływ potencjału lokalnego na rozszczepienie ekscytonowe w CdMnTe*
Advisor: prof. dr hab. Andrzej Twardowski
- High School: II Liceum Ogólnokształcące im. Stefana Batorego w Warszawie

2 Information on previous employment

- 2014 — present: assistant professor at Laboratory of growth and physics of low dimensional crystals SL3, Institute of Physics, Polish Academy of Sciences
- 2004 — 2014: adjunct at Laboratory of growth and physics of low dimensional crystals SL3, Institute of Physics, Polish Academy of Sciences
- 2003 — 2004: post-doc at Universidad Autónoma de Madrid in the group of prof. Luis Viña, Spain
- 1997 — 2003: Ph. D. student at University of Warsaw, Faculty of Physics

3 Bibliometric data

I have published 65 research papers, 55 after obtaining the Ph.D. degree. According to *ISI Web of Knowledge* from January 24th, 2017:

- Hirsch factor $H = 12$
- Number of citation without autocitations 346
- Total *Impact Factor* is 125

The articles were published in such international journals as:

- *Physical Review B* 11 articles
- *Nanotechnology* 2 articles
- *Applied Physics Letters* 4 articles
- *Journal of Applied Physics* 2 articles
- *RSC Advances* 2 articles
- *Nano Letters* 1 article

Moreover, I have co-authored a chapter in a review book *Molecular Beam Epitaxy: From Research to Mass Production* (Elsevier, 2012) entitled *Molecular Beam Epitaxy of Semimagnetic Quantum Dots*.

Other forms of research publications:

- 40 talks at conferences, workshops, and symposia, 27 given personally, 6 invited talks.
- 60 posters, 23 presented personally.
- 12 seminars given at Polish universities.

4 Scientific achievement being the basis of the habilitation procedure

The scientific achievement, in accordance with the **art. 16 paragraph 2 of the Act of March 14th, 2003, concerning the scientific degrees and titles (Dz. U. no. 65, item 595, as amended)**, is the series of publications entitled:

Manipulation of exciton state in a single cadmium telluride quantum dot

- H1. **Ł. Kłopotowski**, M. Goryca, T. Kazimierczuk, P. Kossacki, P. Wojnar, G. Karczewski, and T. Wojtowicz, *Dynamics of charge leakage from self-assembled CdTe quantum dots*, Applied Physics Letters **96**, 201905 (2010).
- H2. **Ł. Kłopotowski**, Ł. Cywiński, P. Wojnar, V. Voliotis, K. Fronc, T. Kazimierczuk, A. Golnik, M. Ravaro, R. Grousson, G. Karczewski, and T. Wojtowicz, *Magnetic polaron formation and exciton spin relaxation in single $Cd_{1-x}Mn_xTe$ quantum dots*, Physical Review B **83**, 081306R (2011).
- H3. **Ł. Kłopotowski**, V. Voliotis, A. Kudelski, A. I. Tartakovskii, P. Wojnar, K. Fronc, R. Grousson, O. Krebs, M. S. Skolnick, G. Karczewski, and T. Wojtowicz, *Stark spectroscopy and radiative lifetimes in single self-assembled CdTe quantum dots*, Physical Review B **83**, 155319 (2011).
- H4. K. Kukliński, **Ł. Kłopotowski**, K. Fronc, M. Wiater, P. Wojnar, P. Rutkowski, V. Voliotis, R. Grousson, G. Karczewski, J. Kossut, and T. Wojtowicz, *Tuning the inter-shell splitting in self-assembled CdTe quantum dots*, Applied Physics Letters **99**, 141906 (2011).
- H5. **Ł. Kłopotowski**, *Charging Effects in Self-Assembled CdTe Quantum Dots*, Acta Physica Polonica A **120**, 819 (2011).
- H6. **Ł. Kłopotowski**, Ł. Cywiński, M. Szymura, V. Voliotis, R. Grousson, P. Wojnar, K. Fronc, T. Kazimierczuk, A. Golnik, G. Karczewski, and T. Wojtowicz, *Influence of exciton spin relaxation on the photoluminescence spectra of semimagnetic quantum dots*, Physical Review B **87**, 245316 (2013).
- H7. **Ł. Kłopotowski**, K. Fronc, P. Wojnar, M. Wiater, T. Wojtowicz, and G. Karczewski, *Stark spectroscopy of CdTe and CdMnTe quantum dots embedded in n-i-p diodes*, Journal of Applied Physics **115**, 203512 (2014).
- H8. **Ł. Kłopotowski**, P. Wojnar, S. Kret, M. Parlińska-Wojtan, K. Fronc, T. Wojtowicz, and G. Karczewski, *Engineering the hole confinement for CdTe-based quantum dot molecules*, Journal of Applied Physics **117**, 224306 (2015).
- H9. **Ł. Kłopotowski**, P. Wojnar, Ł. Cywiński, T. Jakubczyk, M. Goryca, K. Fronc, T. Wojtowicz, and G. Karczewski, *Optical signatures of spin-dependent coupling in semimagnetic quantum dot molecules*, Physical Review B **92**, 075303 (2015).

4.1 Introduction — from epitaxy to nanostructures

The development of epitaxial crystal growth methods that occurred in the seventies allowed producing semiconductor films with thickness that could be controlled within a single atomic layer. These techniques were first employed to grow heterojunctions and quantum wells — structures in which quantization of motion in the direction perpendicular to the layer was observed. These discoveries lead to a major breakthrough in electronics and optoelectronics. They allowed to, e. g., drastically decrease the size of transistors and resulted in development of semiconductor lasers. Devices which are ubiquitous today, like microchips or CD/DVD players, were made possible by the discoveries of epitaxial techniques that took place forty years ago.

Observation of the quantization of electron motion in quantum wells inspired scientists to look for structures, in which the quantization would occur also in two and three dimensions. That is how the field of nanotechnology started. It is devoted to growth, studies, and applications of semiconductor objects with a size comparable to electron de Broglie wavelength. Electronic and optical properties of such *nanostructures* is governed by the laws of quantum mechanics. Fabrication of such structures allowed to discover effects particular to reduced dimensionality, such as the quantum Hall effect.

The subject of this dissertation are quantum dots (QDs) — nanostructures in which the motion is quantized in three dimensions. One of the first attempts to produce such structures took place in mid-eighties. This early approach was based on processing of quantum wells by lithographic masking and etching to produce lateral confinement [1, 2]. Three dimensional quantization of motion was demonstrated in resonant tunneling measurements in such structures [3]. However, optical properties of such QDs were found to be determined by the surface states introduced during etching. These states gave rise to nonradiative recombination channels and generated significant electrostatic disorder in the dot vicinity. The second family of QDs studied in the late eighties and early nineties were structures formed on the rough interface of a quantum well. In this case, the lateral confining potential is due to well width fluctuations with dimensions on the order of tens of nanometers. These fluctuations lead to a local potential minimum, confining the carriers in three dimensions. One of the first observations of the photoluminescence (PL) spectrum of a single QD was reported for such a structure [4]. Good optical properties of these so called natural QDs allowed to demonstrate fundamental optical properties of zero-dimensional semiconductor nanostructures. It was shown that the emission lines are extremely narrow [4] because of decoupling of the fully quantized electronic states from phonons [5].¹ Furthermore, it was demonstrated that the QD shape anisotropy leads to splitting of the exciton ground state and a linear polarization anisotropy of the PL lines [6]. Moreover, the influence of electric field on the transition energies was discussed. An energy shift due to quantum confined Stark effect and a transition broadening due to shortening of the exciton lifetimes were demonstrated [7]. Also, the exciton coherence time was measured [8]. Despite these successes, the natural QDs are poorly suited for applications and more advanced studies. The fabrication process is virtually impossible to control and a shallow confining potential leads to an easy thermal ionization of carriers. As a result, the properties of these dot could only be studied up to few tens of Kelvin.

The third method of producing a three dimensional carrier confinement for quantum well carriers is electrostatic gating of a two-dimensional electron gas [9]. Deposition of electrodes on the sample surface allows not only to confine the carriers but also to control the number of electrons in such QDs. Investigations of such structures showed that the charging spectra are governed by a Coulomb blockade [9]. It was also possible to controllably charge double and triple QDs. More importantly, the ability to electrically tailor the properties of such a system allowed to perform an initialization and coherent control of a two electron state and measure the electron coherence time. These experiments were conducted in view to apply the gated QDs in quantum computations, in which the electron spin state constitutes a quantum bit (a qubit)

¹More specifically, due to Dirac delta-like density of states, electron-phonon scattering is suppressed because of the lack of final electronic states for this process.

[10]. The studies of gated QDs provided a broad insight into the spin properties of semiconductor nanostructures [11]. On the other hand, optical properties of such structures were not studied, mainly due to the nature of the electrically driven confinement provided only for carriers of one sign.

The most promising structures for optical manipulation and readout of their quantum properties are QDs grown epitaxially in the Stranski–Krastanow mode [12]. This growth occurs when on top of material A a layer of lattice mismatched material B is deposited. If the lattice constant of B is greater than for A, B grows pseudomorphically and accumulates elastic energy resulting from strain. Above a certain thickness, lowering of the elastic energy occurs via formation of dislocations. Under certain conditions and for thicknesses below the critical one, the elastic energy can also be relaxed at the expense of surface energy, i. e., by forming dangling bonds on the surface of B. Such a mechanism leads to formation of three dimensional islands on top of a two dimensional wetting layer. Since the movement of B atoms inside the island is free, the strain is partially relaxed and the lattice constant at the top of the island tends to the value characteristic for the unstrained B material.

Quantum dots grown by the Stranski–Krastanow mode, the self-assembled QDs, exhibit excellent optical properties. Since these structures are grown in the matrix of another bulk semiconductor, it is possible to externally tailor their properties. For example, the choice of the barrier material allows to tune the depth of the confining potential. Growth of the QDs inside a photonic structure provides a path to control the radiative lifetimes via the Purcell effect. Furthermore, the strain fields emerging from one QD layer to the covering barrier cause a nucleation of a top QD layer, spatially correlated with the bottom one [13]. This allows to fabricate pairs of coupled QDs [14] and even QD supercrystals [15]. Moreover, deposition of electrodes on top of the bulk semiconductor allows to apply an electric field and investigate charging effects [16, 17], the quantum confined Stark effect [18, 19, 20], and fabricate light emitting diodes. The studies reported in the present dissertation were conducted on QDs fabricated with the Stranski–Krastanow method. Before discussing their fundamental properties and potential applications, I will describe two other fabrication techniques and discuss their advantages with respect to the self-assembled QDs.

The main disadvantage of the self-assembled dots is related to their spontaneous formation. The nucleation occurs where the local density of B atoms exceeds a critical value. Thus, it is very difficult to precisely position these QDs. Another factor limiting the device applications of self-assembled dots is their inhomogeneity resulting in significant inhomogeneous broadening of the ensemble spectrum. The inhomogeneity in size and chemical composition translates into inhomogeneous distribution of confinement energies. One of the methods employed to circumvent these issues is to grow the QDs inside nanowires fabricated via the vapor–liquid–solid technique [21]. The nanowire growth is catalyzed by gold nanoislands forming an eutectic with the substrate material. Elements delivered in gas form saturate the eutectic which is followed by crystallization of the nanowire below the gold nanoisland. The nanoislands can be precisely positioned via electron beam lithography, allowing to grow regular, homogeneous nanowire arrays [22]. The QD position is inherited from the nanowire allowing to attain regular arrays of similar QDs. Moreover, tailoring the nanowire shape it is possible to enhance the efficiency of photon collection from such QDs [23]. For self-assembled QDs this efficiency would have to be tailored by multistep fabrication of photonic structures.

A separate family of QDs are the so called colloidal QDs [24]. These nanostructures are obtained by wet chemistry in a solution and exhibit relatively good homogeneity as the size is controlled by reaction time. The main source of nonradiative recombination are surface states which can be passivated by either an organic or inorganic shell. These methods ensure a high quantum yield of colloidal QDs. Moreover, the size of these dots is much smaller, the diameters are in the range between 2 and 10 nm. This allows tuning of the quantum confinement which in turn enables covering of a broad spectral range with a single material. As a result, colloidal QDs

are applied as light emitting diodes (QLEDs) and in displays. Moreover, these structures can be relatively easily functionalized — a property which lead to numerous applications as biological markers.

4.2 Properties and potential applications of quantum dots

In this chapter, I will discuss some of the properties of quantum dots and the resulting potential applications. The purpose of this chapter is to serve as a background to the studies reported as the dissertation.

As mentioned above, the QD size is comparable to the electron de Broglie wavelength and thus the electron motion is quantized in three dimensions. The density of states becomes discreet and as a result the interaction of carriers with the environment is suppressed compared to higher dimension systems such as quantum wells. The characteristic consequence of this decoupling are narrow PL linewidths [4, 25]. In the case of quantum wells, the line broadening is strongly influenced by the interaction of carriers with phonons. For carriers confined in QDs, this interaction is weakened [5] and the PL linewidths at temperatures below ~ 20 K are only slightly broader than expected from purely radiative broadening. This broadening is mostly determined by the fluctuating electrostatic environment shifting the exciton energies via the Stark effect [26]. The narrow linewidths indicate almost complete decoupling from phonons at low temperatures and thus a strictly zero-dimensional density of states.

The zero-dimensional density of states provides also a possibility to employ QDs as non-classical light sources. Since for one excitation cycle only one exciton can be present in a QD, one cycle corresponds to exactly one photon. This allows to use the dots as sources of single photons on demand [27]. Thus, the photons emitted by QDs are described by a different statistics than lasers or thermal sources. Single photon sources are crucial for realization of quantum cryptography protocols, e. g., the BB84 protocol, which relies on a train of single photons emitted with particular polarizations in particular basis. In a laboratory, BB84 can be realized by attenuating a laser source (emitting photons with Poisson statistics). However, in this case there is always a dominating probability of emitting zero photons per cycle and such sources are inherently very weak. In this respect, the QDs are promising for applications in real devices.

One of the consequences of the epitaxial growth is a shape asymmetry of the QDs. The lateral sizes, the diameters, are in the range 10–30 nm, while the heights are between 2 and 5 nm. The shape, depending on growth conditions can be rather pyramid-like or lens-like. As a consequence of the size anisotropy, it is usually assumed that the confining potential along the growth axis (z axis) can be approximated by a rectangular well, while for the in-plane directions (x and y axes) it is parabolic. For a carrier with mass m_* it is given by: $V(x, y) = V_0 + m_*\omega^2(x^2 + y^2)$. The resulting level structure is that of a harmonic oscillator: $E_{n_x, n_y} = \hbar\omega(n_x + n_y + 1)$ — see Figure 1. Quantization along z results in a repetition of these levels at much higher energies. In practice, these state, if exist, are usually neglected. The rotational symmetry of the lateral potential makes the z component of the orbital momentum a good quantum number. Thus, the subsequent confined states are labeled in analogy to atomic physics as s , p , d , f ... Including spin, the degeneracies of these states are 2, 4, 6, 8..., i. e., smaller than for atoms. The reduced degeneracies are a direct consequence of the reduced QD symmetry, the asymmetry between the in-plane and vertical directions.²

The splitting between different shells, defined as Δ_{sp} is thus related to the lateral dot size.

²The discussion presented here suggests that the QDs exhibit a cylindrical symmetry. In reality, taking into account the underlying crystal structure as well as the anisotropy of strain and shape, the symmetry is much lower, which leads to further lowering of the degeneracies. For the exciton ground state, the anisotropic electron-hole exchange interaction leads to a splitting and mixing of spin states, and results in a linear polarization of the emission lines [6, 28, 29]

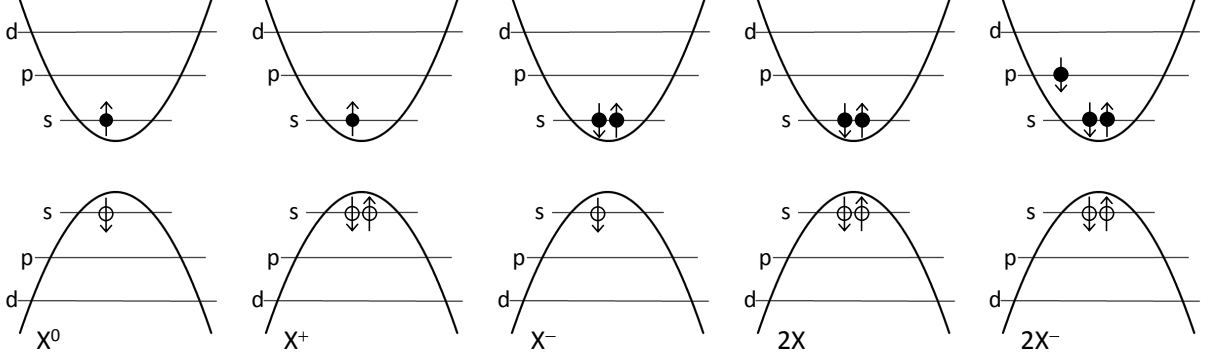


Figure 1: Examples of spin configurations for five excitonic complexes denoted below the schemes. Full (empty) points denote electrons (holes). The parabolas schematically denote the in-plane confining potential. Equally spaced bound states are labeled according to the atomic convention — see text.

The values of Δ_{sp} can be obtained in a PL measurement: increasing the excitation density, one can populate higher shells and observe the recombination from these excited states.³

At small excitation densities, when only the s shell is filled, it is possible to create four different excitonic complexes (see Figure 1): the neutral exciton (an electron-hole pair, X^0), positively charged exciton (trion X^+ with two holes and an electron), a negatively charged exciton (trion X^-) and a biexciton ($2X$ with two electron-hole pairs). Since carrier capture is a stochastic process and occurs on timescales much shorter than a typical PL integration time (~ 1 s), the optical transitions related to these complexes can coexist in the spectrum. Identification of the transitions is not trivial, since depending on the dot morphology the hierarchy of binding energies can be different. Photoluminescence allows to evaluate spectroscopic shifts ΔE_χ for a given complex χ , as $\Delta E_\chi = E(X^0) - E(\chi)$, where $E(\chi)$ is the PL energy of the complex χ . The values of ΔE_χ depend on the Coulomb interactions between the carriers in the initial and final states of the transition. The spectroscopic shifts can be evaluated by taking into account the interaction in the Hartree-Fock approximation. For the complexes constructed from s -shell carriers, one gets [30]:

$$\begin{aligned}\Delta E_{X^+} &= V_{eh} - V_{hh} \\ \Delta E_{X^-} &= V_{eh} - V_{ee} \\ \Delta E_{2X} &= 2V_{eh} - V_{hh} - V_{ee} ,\end{aligned}\tag{1}$$

where V_{ij} denotes a Coulomb integral for interaction between carriers i and j , whose motion is described by wave functions, respectively, $\varphi_i(\mathbf{r}_i)$ and $\varphi_j(\mathbf{r}_j)$. It is given by $V_{ij} = e^2 \int \int |\varphi_i|^2 (1/r_{ij}) |\varphi_j|^2 d^3\mathbf{r}_i d^3\mathbf{r}_j$, where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. This simple approach allows to predict the transition sequence for most of the InAs QDs. For morphologies occurring most often, the hole, owing to its larger mass, is more strongly bound than the electron and, thus, $V_{hh} > V_{eh} > V_{ee}$. Indeed, usually the observed transition sequence is $E(X^+) > E(X^0) > E(X^-)$ [16, 17, 31, 32]. In the description of higher charge states, it is necessary to include the energies of exchange interactions, which lead to multiplets of transitions related to different spin configurations in the initial and/or final states. The Hartree-Fock approximation does not take into account Coulomb correlations, which shift the transitions energies down [31, 30]. As I will show below, these effects are crucial for understanding of the transition sequence in QDs of cadmium telluride.

Placing the QD in the space-charge layer of a Schottky diode allows to control the dot charge state and identify the respective optical transitions. Controllable charging occurs by tuning the

³Alternatively, the information on Δ_{sp} can be obtained from capacitance spectroscopy, where subsequent maxima reflect populating the QDs with carriers. This method provides additional information on energy scales related to the Coulomb blockade.

gate voltage and shifting the Fermi level E_F with respect to the energy of the confined state. When E_F is tuned to resonance with the confined carrier state, a carrier can be injected from the reservoir to the QD by tunneling through the separating triangular barrier — see Figure 2. The carriers are injected sequentially, one by one, because of the Coulomb blockade: an injected carrier increases the electrostatic barrier for the injection of a next one. First observation of this process was performed by means of capacitance spectroscopy on an ensemble of dots [33]. This was followed by the demonstration of the controllable charging in a single dot PL measurement [16]. As the gate voltage is tuned, the PL spectrum undergoes abrupt, step-like changes. These steps are a consequence of charging events, which lead to changes in transition energies. Charge states may coexist if the tunnel coupling between the reservoir and the QD is weak and the tunneling time is longer than the exciton lifetime [34].

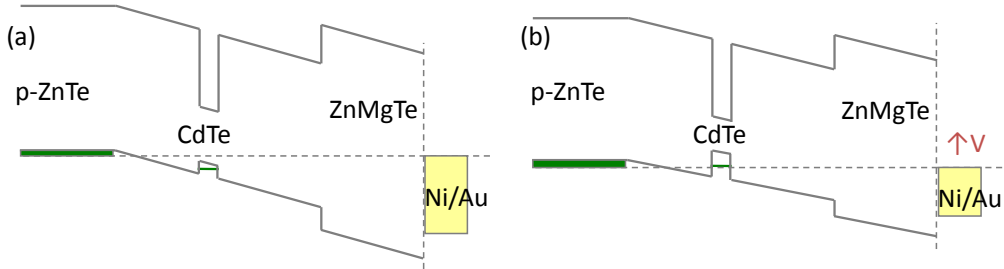


Figure 2: Band extrema in *p-i-Schottky* diodes investigated in the presented dissertation. *p*-type ZnTe buffer layer constitutes the hole reservoir. CdTe QDs are grown in a ZnTe matrix. A nickel/gold layer evaporated on top of the sample is the Schottky gate. An additional barrier of $\text{Zn}_{1-y}\text{Mg}_y\text{Te}$ prevents the carriers from escaping into the metal. (a) Under strong reverse bias, the Fermi level lies above the confined hole state. (b) Application of a smaller bias allows to tune the hole state to resonance with the Fermi level enabling the injection of the hole into the dot through the triangular tunnel barrier.

Controlling the QD charge state opened up a vast field of studies. The analysis of PL spectra corresponding to particular occupancies allowed to determine how the confined states are filled and which spin configurations constitute the ground state. In atoms, these effects are governed by the Aufbau principle and the Hund's rule, respectively. For self-assembled QDs, it was shown that these rules are fulfilled only for electrons [32]. For holes significant deviations occur resulting from strong repulsion between these carriers. Controlling the charge state allowed also to investigate dots with just one carrier. The electron spin state in such a system was investigated in view of applying it in quantum information processing [35, 36]. Full coherent control of such a single qubit was demonstrated optically employing the electron-trion transition [37]. It was shown that the decoherence in this system results from hyperfine interaction of the carrier spin with the fluctuating spins of the nuclei of atoms building the dot [38, 39]. One of the approaches to mitigate the influence of the hyperfine interaction was to obtain the control over nuclear spins. Preparing a dot in a charge state with a single electron allowed to demonstrate a spin transfer from the carrier to the nuclei leading to creation of a dynamic nuclear polarization [40, 41]. The studies also allowed to show that the hyperfine interaction for holes is about 10 times weaker than for electrons [42].

Placing the dot inside a diode structure not only allowed to precisely tune the charge state, but also provided an electric field for the studies of the quantum confined Stark effect [18, 7, 19, 43, 20]: the electric field-induced shifts of the emission lines measured in PL or absorption lines measured by photocurrent spectroscopy. Quantitative analysis of these shifts provided data on the charge distributions inside the dots. These distributions are a consequence of the QD morphology so the analysis of the Stark shifts allowed to relate the dot shape and composition with spectroscopic features. In particular, it was discovered that under zero electric field, the centers of gravity of electron and hole wave functions are vertically offset [43]. It was also shown how the charge distributions change upon additions of subsequent carriers [20].

Applying a large reverse bias results in a dissociation of the exciton and tunneling of one of the carriers out of the dot. Subsequent injection of the carrier from the reservoir leads to recombination and photon emission. Thus, by synchronizing bias and laser pulses it is possible to attain a controllable separation of electrons and holes and their subsequent recombination. This procedure can be applied to studies of writing, storage, and readout of charge from the QDs. Indeed, it was shown that the charge can be stored for timescales on the order of seconds, i. e., exceeding by a factor of 10^9 the exciton lifetime [44]. This ability was later applied to store spin-polarized electrons and readout the temporal decay of the spin polarization [45]. Writing and readout of the electron spin allowed to study the mechanism of the longitudinal spin relaxation. The dependence of the T_1 relaxation time on external magnetic field lead to a conclusion that the process is dominated by scattering on phonons allowed by spin-orbit-driven admixtures to the Zeeman split spin states [45, 46].

Further possibilities of tailoring the carrier states in QDs are provided by fabricating pairs of coupled QDs. The electric field can be used to tune the carrier states to resonance, whereupon the tunnel coupling leads to a hybridization of the wave functions [14, 47]. Using the atom analogy, pairs of coupled dots can be seen as molecules. At the resonance, carrier wave functions become even and odd linear combinations of single dot wave functions, i. e., form the binding and antibinding orbitals. In a PL measurement, the coupling can be identified by observing an anticrossing of transitions for excitons with carriers in the same dot (direct exciton) or in adjacent dots (indirect exciton). Such quantum dot molecules (QDMs) offer additional possibilities to manipulate the carrier orbital wave function. Indeed, the double dots are a model system of coupled qubits. Manipulation of a two-electron state in a QDM and a creation of an entangled state was demonstrated [48]. It was also shown that presence of a carrier in one of the dots influences the optical response of the other dot. Therefore, a sort of conditional dynamics, or a logic gate was demonstrated as the measurement result on one dot was conditional on the state of the other dot [49].

Another system providing a testbed for spin manipulation on the nanoscale are QDs containing magnetic ions. Historically, the first such nanostructures were QDs built from compounds of group II and VI elements with manganese ions replacing the group II cations [50]. The Mn^{2+} ions are incorporated as isoelectronic dopant. Half filled d shell of the ion introduces a magnetic moment $S = 5/2$. The exchange interaction between S and the band carrier spin leads to a giant amplification of magnetooptical effects. For example, exciton Zeeman splitting can be enhanced (at sufficiently low temperature and proper Mn concentration) by a factor of 100 compared to the direct Zeeman interaction of the carrier with the field. Semiconducting compounds with transition metal ions — diluted magnetic semiconductors [51] — are studied since the seventies. Nanostructures of these materials extend the possibilities of tailoring their properties and allow to study novel fundamental effects related to the spin degree of freedom.

The final frontier in the miniaturization of information processing devices is to store and readout the information from a single atom. For cadmium telluride QDs with *exactly one* Mn^{2+} ion it was shown that the ion-exciton interaction leads to a characteristic sextet of lines in the PL spectrum related to the six projections of the ion spin on the quantization axis [52]. It was also demonstrated that the ion spin can be optically oriented [53, 54]. First studies on electrical control of the ion spin state involving coupling of S with the carrier spin were also reported [55].

Semimagnetic QDs with a large (>20) number of Mn^{2+} ions exhibit entirely different properties. In this case, the fluctuations of the ion spin state lead to significant broadening of the PL transition due to the exchange interaction of the total ion spin \mathbf{S} with the exciton [56]. Thus, the total spin state as well as its temporal fluctuations are imprinted into the PL spectrum. This allows to study how these fluctuations depend on external factors. It was shown that application of a magnetic field leads to suppressed fluctuations when the Zeeman energy between the split spin states is larger than the energy of thermal excitations [56]. The ion-exciton exchange interaction leads also to another effect, interesting with respect to information processing. In this system,

the exchange energy is minimized by a spontaneous development of a magnetization of the Mn^{2+} ions [50]. This occurs as a result of an exchange field created by the exciton, so the magnetization develops within the exciton volume. Such an entity — the exciton magnetic polaron — was also investigated in system of higher dimensions. Its static and dynamics properties were accessed by measuring a redshift of the exciton transition, which was related to the formation of the polaron [57]. In the case of quantum wells, the redshift contains a contribution from exciton localization [58]. In QDs, the exciton is inherently localized by the confining potential so the studies on polarons were free of the localization contribution. Polaron formation in semimagnetic dots was demonstrated and the timescale of this process was estimated [59]. From the point of view of fundamental studies of magnetic properties at the nanoscale as well as for applications in spin electronics, it would be desirable to controllably develop the magnetization with light or bias voltage. Theoretical studies showed that the magnitude of the magnetization strongly depends on the QD occupation. For a completely filled shell, carrier spin $s = 0$ and thus the magnetization vanishes. It attains a maximal value for a half filled shell [60]. Thus, by controlling the charge state of a semimagnetic dot it should be possible to turn the magnetization on and off. Experimental works have shown that circularly polarized excitation, and thus creation of spin polarized excitons, leads to magnetization with a corresponding orientation with respect to the quantization axis [61]. These results suggest that under certain conditions, exciton spin relaxation is slower than polaron formation.

In this dissertation, I will present results of PL studies on CdTe dots with multiple Mn^{2+} ions. For completeness, it is necessary to mention that the II–VI compounds are not the only material system studied in the context of magnetic dopant properties and their manipulations in QDs. InAs QDs with single Mn^{2+} ions were also investigated [62]. The spectroscopic features are in this case very different from the II–VI material since the dopant is not isoelectronic and introduces a localized hole. For II–VI compounds different than CdTe it was expected that introducing manganese will lead to significant quenching of the PL efficiency via the excitation transfer to the manganese d -shell electrons and PL emission via the internal transition of the Mn^{2+} ion. Indeed, the studies on CdSe QDs with Mn^{2+} ions were conducted on specially tailored structures, which was aimed at assuring that the internal transition energy lied above the QD transition [59]. However, subsequent studies revealed that introduction of a *single* dopant does not affect the exciton lifetime [63]. This lead to a conclusion that in such a case the excitation transfer is negligible and does not influence the PL efficiency. Furthermore, it was demonstrated that other transition metal ions can be incorporated into the QDs. Spectroscopic features related to single cobalt, iron, chromium, and copper were then described.

4.3 Motivation — cadmium telluride quantum dots

The principal goal of the reported studies was to obtain a control over exciton states in cadmium telluride QDs. This ability is the basic requirement for employing the dots as components of advanced devices. Attaining such a control is also an achievement in itself. It proves the ability to manipulate the electronic, optical, and magnetic properties of nanoobjects. It shows that the quantum properties can be tailored to special needs by the fabrication techniques and subsequent post-processing. Therefore, the ability to control the properties of nanostructures makes them in this respect superior to natural nanostructures, like atoms, whose properties are to a large extent fixed.

The most straightforward approach to such a control is modification of the nanostructure morphology. The easiest way is to change the nanostructure size, which will translate to the change of the energy level structure. This is not only a fundamental problem. The energy separation between the ground and the first excited state, the Δ_{sp} splitting, is one of the parameters determining the rate of longitudinal electron spin relaxation [45, 46]. To tune the lateral size in InAs QDs, usually the technique of *indium flush* is applied. In this method, the excess of indium

is "flushed" by increasing the growth temperature [64]. When the present studies were being undertaken, no such control of the inter-shell splitting in II-VI QDs was known.

The majority of studies devoted to controlling the carrier states in QDs were focused on InAs-based nanostructures. Historically, the domination of these structures was related to a large community of researchers developing III-V crystal growth techniques and to the availability of titanium-sapphire lasers, which allowed for advanced spectroscopic studies. There is much less research groups studying the epitaxial techniques of the II-VI compounds. Initially, there was also the lack of tunable laser sources in the orange-yellow part of the spectrum — where the excitonic absorption bands of CdSe, ZnTe, or CdTe nanostructures lie. It is important to note that II-VI compound QDs offer certain advantages over the better known III-V nanostructures. For example, as mentioned above, the qubit decoherence in InAs QDs is governed by the hyperfine interaction of the carriers with the nuclei. The magnitude of this interaction is proportional to the nuclear spin I and to the abundance of the non-zero spin isotopes. For indium, gallium, and arsenic, 100% of the nuclei carry spin, respectively, $I_{\text{In}} = 9/2$, $I_{\text{Ga}} = 3/2$ i $I_{\text{As}} = 3/2$. Meanwhile, for cadmium, zinc, and tellurium, only respectively 25%, 4%, and 8% of nuclei carry spins $I_{\text{Cd}} = 1/2$, $I_{\text{Zn}} = 5/2$ i $I_{\text{Te}} = 1/2$, respectively. It is thus expected that hyperfine-driven decoherence times for QDs built from these elements would be longer. Unfortunately, the studies of hyperfine coupling in II-VI compounds are scarce. One of the tools for these studies is the measurement of the energy of trion transitions, for which a stable $\pm 1e$ charge state is required. It is therefore important to develop methods for charge control in these nanostructures. Sequential carrier injection relies on the Coulomb blockade in a field-effect structure. Another benefit from developing such structures is the possibility to observe the quantum confined Stark effect. These studies provide information on QD morphology, the resulting charge distributions, and also on the nature of Coulomb interactions governing the energies and intensities of optical transitions. Placing dots in electric field also allows to develop devices for charge storage and storage and readout of the spin state, which can provide data on spin relaxation mechanisms. The above discussion shows that fabrication of charge tunable devices with CdTe QDs would open a large field of studies. However, at the time where the studies reported here were undertaken, there were only a few early reports on the Stark effect and charging in CdSe QDs [65, 66] and one on the electrical control of the spin state of CdTe dot with a single Mn^{2+} ion [55]. Additional motivation for developing the field-effect structures was the possibility to go further with these devices: fabrication of light emitting diodes, charge storage devices, structures for photocurrent measurements etc.

The second important advantage of CdTe QDs over III-V dots is the feasibility of doping with transition metal ions. As mentioned above, there are reports on one or two Mn^{2+} ions in an InAs QD. However, doping with a larger number of ions is hindered by low solubility of manganese in III-V compounds. The studies of QDs with many magnetic ions are carried on nanostructures of $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ or $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$. From the spectroscopist point of view, the problem with the selenide dots is the relatively low PL efficiency due to the excitation transfer to the Mn^{2+} ion described above. In order to assure a large PL intensity it is necessary to lower the PL transition energy by growing sufficiently large QDs. In the case of telluride QDs, the detrimental transfer is less efficient since due to smaller CdTe band gap the exciton energies are in this case smaller.

The studies on the semimagnetic $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ QDs would also benefit from the ability of charge control. The ultimate goal of the presented studies was to attain the electrical control of the magnetization in these dots by sequential filling of the electron states and turning the polaron effect on and off, as predicted by theory. However, before such a device could be fabricated, it was necessary to understand the mechanism of polaron formation, evaluate the timescales for the underlying processes and, in particular, measure the polaron formation time τ_f . Before undertaking these studies, the only measurement of τ_f was conducted on the ensemble of QDs, where the temporal redshift of the PL peak was identified as the development of the polaron [59]. However, such a shift contains also a contribution from exciton transfer from small to large

dots [67]. Also, because of the significant inhomogeneous broadening of the ensemble spectrum, it was impossible to measure small energy shifts. Providing precise values for τ_f for different manganese molar fractions x required studies on single QDs.

Another subject which was little investigated, when I was starting the reported studies, was the fabrication and studies of coupled QDs. The advantages of the II–VI QDs with respect to the III–V counterparts quoted above can also be exploited in the case of QDMs and thus legitimize undertaking the studies of CdTe–based QDMs. Moreover, new procedures for tuning the coupling in these structures open up due to doping with Mn^{2+} ions. Namely, tuning the coupling can be achieved with magnetic field. Since the Zeeman effect removes the spin degeneracy, such coupling would be spin dependent.

Another motivation for the presented works was to understand the differences between CdTe and InAs QDs and how they influence the PL properties such as the sequence of the transition lines and the lifetimes of the particular excitonic complexes. When I was starting these studies, such issues were barely addressed.

4.4 Manipulation of exciton state in a single cadmium telluride quantum dot

4.4.1 Charge tuning

In order to attain the charge tunability for CdTe QDs, we investigated two types of structures: Schottky diodes and p – i – n diodes. The Schottky diodes consisted of a nitrogen doped p –type ZnTe buffer layer with the QDs embedded into a ZnTe barrier. On top of the sample a nickel/gold gate was evaporated. These samples were designed in analogy to the structures employed for charge tunability in InAs QDs. Deposition of the metallic gate results in a built-in electric field. Biasing the structure results in an additional field. The total electric field is given by $F = (U - U_{bi})/w$, where U and U_{bi} are the applied and built-in voltages, respectively, and w is the width of the space-charge layer. Applying the voltage results in a relative shift of the Fermi level E_F with respect to the confined QD states. When the hole energy is tuned below E_F , a hole is injected from the reservoir (the p –type ZnTe) into the dot across the triangular tunnel barrier (see Figure 2). As a result, abrupt changes in the PL spectrum are expected each time the charge state is changed.

Results of the studies of charging effects in these p – i –Schottky structures are reported in papers H3 and H5. For large reverse biases, we expected negatively charged QDs: the hole levels lie below E_F and thus, the photoexcited holes tunnel out into the reservoir. Indeed for large reverse (negative) biases, we found that the transition identified as the recombination of X^- dominates the PL spectrum. As the bias is shifted toward the forward direction (positive bias), the transition identified as X^0 gains intensity. As the bias is further increased in forward direction, the transition identified as X^+ dominates (see Fig. 1(a) in H3 and Fig. 6 in H5). Increasing the excitation power results in an increased contribution from the $2X$ transition. For CdTe dots grown in ZnTe barriers we found that the transitions from different charge states coexist in the PL spectrum: no clear charging steps associated with carrier injections are resolved. We interpret this effect as resulting from a relatively weak tunnel coupling in these structures: the width of the barrier layer between the QDs and the reservoir was 80 nm. Moreover, the excitation energy in these experiments was sufficiently high to create carriers above the dot excited states. This could have lead to separate capture of electrons and holes. Clear charging steps were observed for samples where the dots were grown into $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{Te}$ barriers (see Fig. 6 in H5). In this case, the reservoir was only 15 nm away from the dots. Moreover, the presence of magnesium raises the barrier height, which additionally stabilizes the charge state.

The second type of structures, the n – i – p diodes consisted of an iodine, n –type CdTe buffer and the QDs in undoped ZnTe covered with p –type ZnTe layer. The advantage of these structures is the lack of the metallic gate, which requires a Schottky contact. The n – i – p diodes are ideally suited for studies of the Stark effect (see below), but the interpretation of the charging behavior

is rather complicated. In this case, the charging occurs as a result of bias tunable capture efficiency of electrons and holes. The results of these studies were reported in H5 and H7. In H7, we reported calculations of tunneling times of electrons and holes made within the WKB approximation. We found that the quenching of the PL spectrum and dominance of the X^- under increasing reverse bias results from tunneling of the holes out of the dots. This process was shown to control the charging behavior: as the tunneling is suppressed under forward bias, the QDs become positively charged.

4.4.2 Coulomb interactions

The changes of the charge states induced by the bias in either the Schottky of $n-i-p$ diodes allowed to unambiguously identify the optical transitions in the PL spectrum from a single CdTe QD. This tool is complementary to the analysis of optical orientation [68] or photon correlation measurements [69], but is free of any *a priori* assumptions. Analyzing the charging effects in CdTe QDs, we found that the transition sequence is always the same, i. e., $E(X^0) > E(X^+) > E(X^-) > E(2X)$. This result is different from the InAs case, where different sequences are observed, and usually $E(X^+) > E(X^0) > E(X^-)$ (see Eq. (1) and the discussion above). In H3, H5, and H7 we showed that the universality of the observed sequence is due to the CdTe QD morphology and the resulting character of the Coulomb interactions. In H5, we discussed the recombination energy of an electron-hole pair $E(N_e, N_h)$ from a dot containing N_e electrons and N_h holes. Beside the single carrier contributions given by the Hartree-Fock approximation, we considered the influence of correlation energies stemming from admixtures of higher orbitals and minimizing the Coulomb energy. Assuming stronger binding of the X^- than the X^+ (as is usually assumed), we showed that the observed transition sequence is reproduced when the correlation energy is larger than the Hartree-Fock term. This allowed us to conclude that the Coulomb correlations are the leading factor that influence the transition energies in CdTe QDs.

The electric field produced in the Schottky or $n-i-p$ diode allows to study some properties of carrier wave functions by analyzing the field-induced shifts, i. e., the quantum confined Stark effect. For experimentally accessible fields, usually a quadratic dependence of transition energy on field is observed. The shifts can be quantified within perturbation theory [19], which gives $E(F) = E_0 - pF + \beta F^2$, where E_0 is the transition energy for zero field and p and β are, respectively, the static dipole moment and exciton polarizability. The p parameter is the spatial separation between the centers of gravity of electron and hole wave functions at $F = 0$. Polarizability β quantifies how easily the electron and the hole can be pulled apart by the field. In H3, H5, and H7 we showed that usually in CdTe QDs $p > 0$. Thus, in absence of electric field, the hole lies above the electron (when looking along the growth axis). For a dot with a translational symmetry we would expect $p = 0$. For pyramid-shaped QD, the lateral potential depth at the bottom of the dot is larger than at the apex. One could thus predict that the hole, as the heavier particle, would lie below the electron [19]. However, for both InAs and CdTe QDs the inverted alignment is observed [43]. The calculations showed that for InAs dots this effect can be caused by intermixing of the indium and gallium atoms. It could be speculated that, analogously, mixing of the cadmium and zinc would lead to the inverted alignment in CdTe dots. By evaluating p for different excitonic complexes, we were able to discuss response of the wave functions to charging with extra carriers. We found that upon charging absolute value of p decreases. The change is greater for the X^+ than for the X^- , which suggests that the hole wave functions undergoes redistributions more easily than electron wave function. This effect can also be understood on the grounds of Coulomb correlations. Wave function distortions require admixtures of higher orbitals. Because of the heavier hole mass, the hole states lie closer to each other than electron states. As we showed in H3, H5, and H7, this facilitates higher orbital admixtures and makes the hole wave function relatively "softer" than the electron wave function.

The analysis of the Stark shifts for tens of QDs revealed that although the case of $p > 0$ dominates, there are dots with a different morphology which lead to the other alignment, i. e.,

with $p < 0$. In H7 we analyzed how the sign of p influences the behavior of spectroscopic shifts ΔE_χ in electric field (see Fig. 4 in H7). We showed that for the most common situation with $p > 0$, for all transitions ΔE_χ decreases with field. For a pyramid-shaped dot we would expect a decrease of ΔE_{X^+} and an increase of ΔE_{X^-} with F : the field increases the Coulomb repulsion as the electron are shifted toward the dot apex and decreases the repulsion as the electrons shift toward the base [70]. Since both ΔE_{X^+} and ΔE_{X^-} decrease with F , we concluded that the dot shape resembles rather a bi-convex lens. For the opposite sign of p ΔE_χ increase with the field, which confirms this conclusion (see discussion in H7).

4.4.3 Exciton lifetimes

Additional information regarding the properties of carrier wave functions can be accessed by analyzing the exciton lifetimes. We found that the decay times for the X^0 PL were in the range between 150 and 350 ps and for a given dot the decay times depended on the charge state (see Fig. 3 in H3). These observations allow to draw conclusions about the character of the carrier confinement on CdTe QDs. In the limit of strong confinement, the wave functions are frozen, determined by the QD morphology while Coulomb interactions are only perturbations. In this limit, the PL lifetimes for X^0 , X^- , and X^+ are expected to be equal and the PL lifetime for the $2X$ is half that of the X^0 , since the biexciton has two decay channels, while the exciton has only one. However, in H3 we presented evidence that upon charging with a hole the PL lifetime is increased; charging with an electron results in a smaller lifetime variation, and the $2X$ lifetime is on average about 0.7 that of the X^0 . These results indicate that the confinement is far from the strong confinement limit: the wave functions undergo redistributions upon charging, which results in the variations of the PL lifetimes. Greater change observed for the X^+ PL lifetime once again indicates that Coulomb correlations in the valence band are strong. Moreover, the value of the PL lifetime itself already shows that the system is not in the strong confinement limit. The lifetime is determined by the oscillator strength, given in this limit by $f = \langle \phi_e | \phi_h \rangle E_P / (2E_{PL})$, where $\phi_{e,h}$ are the electron/hole wave functions, E_P is the energy related to the Kane matrix element, and E_{PL} is the PL energy. Under strong confinement limit we have maximum overlap $\langle \phi_e | \phi_h \rangle = 1$ and for a CdTe QD in a ZnTe matrix the lifetime should be on the order of 1 ns. Shorter lifetimes measured in the experiment do not result from a weaker electron-hole overlap, but from the effect of Coulomb correlations. In this case the exciton wave function is not a simple product of ϕ_e and ϕ_h , but contains a contribution from the relative carrier motion in the QD plane: $\Psi(\mathbf{r}_e, \mathbf{r}_h) = \phi_e(\mathbf{r}_e)\phi_h(\mathbf{r}_h)s(\rho_e - \rho_h)$. The lifetime in this case is proportional to the probability of finding the electron in the same place as the hole, i. e., to $s(0)$. Therefore, we reach a counterintuitive conclusion: weaker carrier confinement leads to a larger oscillator strength [71] and shorter PL lifetimes.

4.4.4 Comparison with III-V quantum dots

The studies of charging effects and PL lifetimes allowed us to capture the fundamental differences between the CdTe dots and their III-V counterparts. These are discussed in H5. The underlying source of these differences lies in the ratio of the exciton Bohr radius to the average QD size. The size of the CdTe QDs is relatively large — the diameters are about 10–20 nm and heights 2–4 nm, while the Bohr radius is only 3.5 nm. Consequently, the properties of these dot resemble rather those of the natural GaAs QDs than those of self-assembled InAs dots. Indeed, for the natural dots a universal transition sequence is observed with the trion lines at lower energies than X^0 and the lifetimes are much longer than estimated for the strong confinement limit.

4.4.5 Charge storage

Quantum information processing requires procedures for electrical storage and readout of the electron state. The structures applied to the fundamental studies reported in H3, H5, and H5

were also employed to demonstrate electron storage. The studies of our storage device were reported in H1. By synchronizing bias and laser pulses, we were able to convert the photons to electrons and store them in a layer of CdTe dots. The charge was then readout with a forward bias pulse, injecting the holes and leading to a electroluminescence peak. We used the amplitude of this peak as the measure of the number of electrons stored at the moment of hole injection.

The described device allowed to study the leakage dynamics of the electrons from the dots. We demonstrated electron storage for times exceeding 10 ms. We showed that the leakage rate is larger for a shallower confining potential, i. e., for larger electroluminescence peak energy. Moreover, the leakage rate decreases with the density of stored charge leading to a non-exponential charge decay. In order to explain this behavior, we pointed out that the stored electrons create an electric field screening the external one. This screening field is time dependent as the electrons leak out of the dots. Consequently, the leakage rate depends on the number of electrons. To reproduce the experimental data quantitatively, we solved a self-consistent rate equation problem taking into account a time-dependent tunneling rate, calculated within a WKB approximation. The results allowed us to reproduce the observed temporal decay of the electroluminescence peak and also its dependence on the emission energy (i. e., the confinement depth), and other storage parameters (see Figs. 3 and 4 in H1).

4.4.6 Tuning the inter-shell splitting

As mentioned above, the easiest way of controlling the QD properties is by tailoring the morphology. We employed this approach in H4 to tune the inter-shell splitting, i. e., Δ_{sp} . We took advantage of the formation mechanism of CdTe dots — a modified Stranski-Krastanow procedure. In this method, a pseudomorphic CdTe layer is grown with a thickness not exceeding the critical value for formation of dislocations. In order to catalyze the dot formation, the two dimensional layer is covered with amorphous tellurium or zinc [72, 73]. By increasing the growth temperature, the amorphous layer is desorbed and the dots are formed because of the changed balance between the elastic and surface energies. For the studies reported in H2, samples with different thicknesses of the CdTe layer were grown.

In the case of InAs dots, Δ_{sp} can be measured directly in the PL spectrum from the QD ensemble. This is possible since the inhomogenous broadening of the ensemble spectrum is in this case smaller than Δ_{sp} . The ensemble of CdTe QDs is more inhomogenous and the opposite is true. Therefore, Δ_{sp} can be only accessed through single dot spectroscopy. To obtain reliable values, analysis of a large statistics is necessary. One method of measuring a single dot spectrum is spectral filtering: observing the PL in the low or high energy tail of the ensemble spectrum. This approach hinders collecting data for a large number of dots and, moreover, the selected dots are inherently specific: either very large or very small. To circumvent these problems, we deposited shadow mask apertures on the sample surface to limit the area of the excitation spot. Apertures with 200 nm in diameter resulted in PL spectra of no more than four QDs. Given a large energy distribution, this allowed to collect a significant statistics of single dot spectra.

With increasing the excitation density, we first observed a linear increase of the X^0 signal and roughly quadratic increase of the $2X$ PL. When the intensities of these transitions start to saturate another set of lines at higher energies appear. These lines are recombinations of carriers from the p shells. The splitting Δ_{sp} was evaluated by taking the energy difference between X^0 and the center of the p transitions band (see Fig. 1 in H4). Δ_{sp} was evaluated for about 100 QDs. We found that as the thickness of the CdTe layer is increased, Δ_{sp} increases. Since Δ_{sp} is directly related to the size of lateral confinement, this result showed how the growth conditions influence the QD morphology and the resulting energy level structure. We interpreted the change in the lateral size as resulting from a different balance of elastic and surface energies (see H4 for details).

The results presented in H4 are also important from the point of view of calculations of carrier wave functions since Δ_{sp} is the crucial parameter that control the Coulomb admixtures of higher

orbitals [74]. Moreover, in H2 we demonstrated that as the excitation density is increased, the emission from subsequent multiexciton states occurs in a cascade. This property is fundamental for applications of QDs as sources of single photons on demand.

4.4.7 Spontaneous magnetization and spin relaxation in QDs with many Mn^{2+} ions

The possibility to study single QDs was the necessary requirement for the studies of magnetization formation in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ QDs with many Mn^{2+} ions. I consciously use the formula for the alloy compound, since the density of Mn^{2+} ions strongly exceeded the situation when one can talk about doping. As a result of our studies, a complete picture of the formation mechanism and the underlying processes was presented in H2 and H6. As mentioned above, the spontaneous formation of magnetization among the paramagnetic Mn^{2+} ions appears as a result of the exchange interaction between the ions and the exciton. The exciton imposes an exchange field and thus the magnetization forms within the exciton wave function. This entity is the exciton magnetic polaron. Since formation of the polaron stems from the tendency of the system to minimize the exchange interaction, the formation is accompanied by a redshift of the excitonic PL. The first questions we wanted to answer were: how fast does the polaron develop and how does it depend on the manganese molar fraction x . We provided the answers in H2. We showed how the PL line from a single $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ QD redshifts with the delay after the excitation with a laser pulse. We found that for $x < 0.03$ it was very hard to observe a redshift. For $0.03 < x < 0.1$ a distinct redshift is observed, but, clearly, the system does not reach equilibrium as the polaron formation in this case is slower than recombination. On the other hand, for $x > 0.1$ we recorded redshifts of about 10 meV with a characteristic saturation at longer delays pointing to a complete equilibration of the system and formation of the polaron. Thus, we found a strong dependence of the polaron formation time τ_f on x .

The second question that required answering for a full understanding of the polaron physics in these QDs considered the hierarchy of relaxation times. Establishing this hierarchy would show whether an optical orientation of the polaron is possible. This problem is important for applications of the semimagnetic dots in prototypical devices using the magnetization as the information carrier. The question can be answered by establishing whether the polaron is formed before the exciton loses its spin polarization or not. We addressed this problem by measuring the temporal decay of the circular polarization of the exciton PL. This allowed us to evaluate the exciton spin relaxation time τ_{sr} . The results of this experiment were reported in H2, where we showed that $\tau_{sr} < \tau_f$ for the whole investigated range of x between 0.01 and 0.2.⁴ The observed hierarchy of relaxation times points to the following polaron formation scenario. The spin of Mn^{2+} ions undergo constant thermal fluctuations, which lead to a fluctuating magnetization. Under absence of the magnetic field — either external created by a coil, B_0 or exchange field created by the exciton, B_{ex} — these fluctuations average to zero. Optical excitation creates an exciton in a dot, which experiences the momentary fluctuation as an exchange field. In this field the exciton relaxes its spin at the direction related to the initial fluctuation. The exchange interaction between the ions and the exciton subsequently amplifies the magnetization within the exciton volume. This leads to decreasing of the energy of the system and eventually to a thermal equilibrium in the exciton- Mn^{2+} ion system. Unless the process is not interrupted by exciton recombination, the magnetization grows during time τ_f after which the equilibrium is attained.

Article H6 shows how the relaxation processes in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ QDs influence the shape of the PL spectrum. We developed a model describing the PL line excited nonresonantly with unpolarized light. Since for a given x the number of Mn^{2+} ions N_{Mn} experiences statistical fluctuations, we decided to use N_{Mn} instead of x as an independent variable. Moreover, since

⁴For a very small number of Mn^{2+} ions in a dot, we may expect an opposite inequality. In particular, studies of dots with a single Mn^{2+} ion revealed that it is possible to orient the ion spin by injecting spin polarized excitons [53, 54]

the dots contained $N_{\text{Mn}} > 20$ ions, their total spin \mathbf{S} could be treated as a classical vector. The interaction of the exciton spin with \mathbf{S} was treated as the sum of the electron–Mn, $s-d$ exchange, and hole–Mn, $p-d$ exchange using a standard Heisenberg Hamiltonian. The exchange constants $N_0\alpha$ and $N_0\beta$ were taken equal to their values for bulk $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$. An important approximation was made regarding the form of the carrier wave functions. We assumed a muffin–tin approximation in which the wave function has a constant value inside the QD volume while vanishing outside: $\Psi_{e,h}(\mathbf{r}) = 1/\sqrt{V_{e,h}}$, where $V_{e,h}$ denote *a priori* different electron and hole volumes.⁵ The approximation, although crude, allows to capture the essential physics behind the exciton–Mn exchange interaction and dramatically simplifies the calculations.

The proposed model allowed to calculate the PL spectra analytically for each of the three relaxation stages. In the first stage, the exciton probes the initial distribution of the Mn^{2+} ions, reflecting their thermal fluctuations. The PL spectrum is, consequently, Gaussian with the linewidth given by the variance of S^z distribution (see Eq. 14–16 in H6). In the second stage, exciton spin relaxation leads to occupation of the low energy configurations of its spin and S^z . As a result the line shape is asymmetric: a Gaussian cut from the high energy side by the Boltzmann distribution of the exciton population (Eq. 19 in H6). At this stage, average magnetization (average S^z) is still zero. In the third stage, Mn^{2+} ions respond to the interaction with the total magnetic field $B = B_0 + B_{ex}$, which leads to a nonzero magnetization. The description is valid for the case when there is no external field and the magnetization is due to the polaron formation under $B = B_{ex}$ and for the case of small N_{Mn} , where the polaron is not formed and the magnetization results from a nonzero B_0 .

The results of calculations are then compared with experimental PL spectra. In particular, we show that indeed the PL line shape changes with time after the excitation as the system relaxes toward equilibrium. For a small number of Mn^{2+} ions the PL line shortly after excitation is symmetric and then acquires an asymmetry as the exciton spin relaxation proceeds. The line redshifts, but the equilibrium is not reached as τ_f is longer than the exciton lifetime. For a dot with a large N_{Mn} the situation is different. Already for the shortest delays we find that the PL spectrum is asymmetric, a consequence of a very fast exciton spin relaxation. As the time delay increases, the line redshifts and becomes symmetric as expected for the fully developed polaron under B_{ex} . The PL line shape analysis confirms the conclusions of H2: (i) both τ_{sr} and τ_f become shorter with increasing the exchange induced exciton splitting and (ii) in the investigated range of Mn molar fractions we find $\tau_{sr} < \tau_f$. The model was also used to fit the steady state PL spectra measured as a function of B_0 for a dot with $x = 0.035$. In this case, at zero field the asymmetry is clearly seen and then with increasing field the line becomes Gaussian as the magnetization is developed under B_0 .

The analysis of the Zeeman shifts and PL linewidths of the exciton PL as a function of B_0 allowed to extract the parameters governing the spectroscopic properties of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ QDs. This allowed us to evaluate the QD volume (expressed in the number of cation sites), the spin temperature of the Mn^{2+} ions, and the number of ions N_{Mn} and show that the magnitude of the exchange field B_{ex} is on the order of a few Tesla. These parameters were obtained for the whole investigated range of molar fractions, from 0.01 to 0.2.

The results presented in H2 and H6 unambiguously demonstrate that in the $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ QDs the *exciton* spin relaxation occurs. This case is different from both InAs and CdTe dots, where the spin relaxation of separate carriers is the dominant mechanism. The question remains what is exactly the role played by the Mn^{2+} ions. The role can be static: in this case the exchange interaction simply assures a magnetic field under which the relaxation occurs via the mechanisms described in other material systems [45, 46]. On the other hand, the dynamic role would invoke a process in which the exciton spin is flipped with a simultaneous change in the

⁵For realistic confinement conditions and because $\beta/\alpha = 4$ we find that it is sufficient to consider an effective QD volume equal to the volume occupied by the hole.

ions spin. Such a mechanism was proposed to govern the electron spin relaxation in quantum wells with $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ barriers [75].

Another interesting question which remains to be addressed is the magnetization dynamics in charged QDs, i. e., the interaction of the Mn^{2+} ions with the trions X^\pm . This area is difficult to access experimentally since the broadening of the PL line hinders the identification of the transitions lines for dots with $x > 0.05$. Moreover, from our unpublished data we conclude that the spectroscopic shifts Δ_{X^-} and Δ_{X^+} decrease with x . This calls for investigations of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ QDs where the charge state is precisely controlled. The first step in this direction was made in H7, where we demonstrated charge tuning for a $\text{Cd}_{0.995}\text{Mn}_{0.005}\text{Te}$ dot.

4.4.8 Molecular coupling in pairs of coupled dots

The expertise and knowledge acquired during conducting the studies described above were used to employ yet another method of tailoring the carrier states in CdTe QDs. By growing two layers of dots we intended to develop between them a tunnel coupling that would lead to hybridization of the orbital wave functions over the two dots. Such an approach was applied for InAs QDs embedded in Schottky diodes. The electric field allowed to tune the carrier states in adjacent QDs to resonance, whereupon the molecular state was formed. Its characteristic fingerprint is an anticrossing of direct and indirect exciton transitions, as discussed in Sec. 4.2.

In H8 we studied analogous structures with CdTe QDs. Combining the PL studies with transmission electron microscopy, we showed that the CdTe dots grown in a double layer in ZnTe barrier are morphologically very different: the top dot is much larger than the bottom one. As a result, the electronic states are strongly detuned and, with the electric field available in our diodes, it is impossible to bring them to resonance. To solve this problem, we proposed a method of engineering the confinement in this double dot structure. By growing the two layers in a material with a larger lattice constant ($\text{Zn}_{1-y}\text{Mg}_y\text{Te}$ alloy) and separating them with a ZnTe barrier, we tuned the amount of elastic energy available for dot formation independently in the two layers. Varying y we were able to obtain a situation in which either the bottom or the top dot exhibited the deeper confinement. This in turn allowed to observe the anticrossings proving the formation of the molecular state.

A completely new mechanism of coupling of the states in the two QDs was presented in H9. In this work, we showed that in the structure with a non-magnetic CdTe dot and a semimagnetic $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ dot, the resonance can be reached by tuning the energies with magnetic field. We investigated pairs of QDs separated with barriers 4 nm or 8 nm wide. We showed that for 8 nm barriers, the tunnel coupling is absent. On the other hand, for the 4 nm barrier we distinguished two types of couplings and described the corresponding spectroscopic features. In the weak coupling, part of the carrier wave function penetrates into the semimagnetic QD, which leads to a *nonresonant* line broadening and increase of the Zeeman splitting. In this case, the wave function penetration is field-independent and, as a consequence, both the observed broadening and increased splitting exhibit a behavior symmetric in B_0 . For a *resonant* coupling, this symmetry is broken: we find that the Zeeman shift is larger for one circular polarization than the other and that the dependence of the linewidth on B_0 is non-monotonic. In order to interpret this counterintuitive behavior and connect it with the formation of the molecular state, we developed a model describing the field dependence of the X^0 PL transition energy and linewidth. The model reported in H6 was the starting point, extended by including the penetration of the wave function from the non-magnetic dot to the semimagnetic one. Fitting the results to the experimentally measured Zeeman shifts and linewidths allowed to disentangle the field dependence of the electron energies for the double dots. We showed that in the resonant field, the wave function hybridizes over the two dots, but this effect occurs only for one spin polarization of electrons. Thus, we deal with a specific, spin dependent coupling.

In H9 we discussed in detail the influence of this coupling on the PL spectra of the coupled dots. In agreement with the results of H2 and H6, we found that the exciton spin relaxation

hinders the observation of an anti-crossing of lines. Indeed, in the PL spectra, the anti-bonding states are absent and we observe only the lower of the anti-crossing lines. Furthermore, the non-monotonic field dependence of the PL linewidth exhibits a maximum at the resonant field, which can be used as a tool for initial verification of coupling.

The described effects are related to the X^0 transition. In Fig. 2(c) in H9, another set of transitions is observed, which we related to the X^- . In this case, the electron coupling leads to a complicated pattern of lines. At the resonance, in the initial state one deals with six spin configurations for the electron pair: two singlets for electrons in the same dot plus a singlet and a triplet for electrons in separate dots. In the final state, the electron occupies either the bonding or the antibonding orbital, so in total there are 12 transitions for each circular polarization. Modeling this situation requires a more detailed knowledge of the structure morphology and the resulting wave function in order to determine the coupling parameters.

As we stressed in the title of H9, the results are general for the whole family of semimagnetic QDs and can be a starting point for further studies of spin dependent couplings in other materials. The presented results prove a fabrication of a novel nanostructure, which opens new possibilities to tailor the spin properties by controlling the wave function overlap between the dots.

References

- [1] K. Kash, *et al.* Applied Physics Letters **49**(16), 1043 (1986). doi: <http://dx.doi.org/10.1063/1.97466>.
- [2] J. Cibert, *et al.* Applied Physics Letters **49**(19), 1275 (1986). doi: <http://dx.doi.org/10.1063/1.97384>.
- [3] M. A. Reed, *et al.* Phys. Rev. Lett. **60**, 535 (1988). doi:10.1103/PhysRevLett.60.535.
- [4] K. Brunner, *et al.* Phys. Rev. Lett. **73**, 1138 (1994). doi:10.1103/PhysRevLett.73.1138.
- [5] D. Gammon, *et al.* Science **273**, 87 (1996).
- [6] D. Gammon, *et al.* Phys. Rev. Lett. **76**, 3005 (1996). doi:10.1103/PhysRevLett.76.3005.
- [7] W. Heller, *et al.* Phys. Rev. B **57**, 6270 (1998). doi:10.1103/PhysRevB.57.6270.
- [8] N. H. Bonadeo, *et al.* Science **282**(5393), 1473 (1998). doi:10.1126/science.282.5393.1473.
- [9] S. Tarucha, *et al.* Phys. Rev. Lett. **77**(17), 3613 (1996). doi:10.1103/PhysRevLett.77.3613.
- [10] J. R. Petta, *et al.* Science **309**, 2180 (2005).
- [11] R. Hanson, *et al.* Rev. Mod. Phys. **79**, 1217 (2007).
- [12] P. Michler, editor. *Single Semiconductor Quantum Dots*. Springer-Verlag (2009).
- [13] Q. Xie, *et al.* Phys. Rev. Lett. **75**, 2542 (1995). doi:10.1103/PhysRevLett.75.2542.
- [14] H. J. Krenner, *et al.* Phys. Rev. Lett. **94**(5), 057402 (2005).
- [15] G. Schedelbeck, *et al.* Science **278**(5344), 1792 (1997).
- [16] R. J. Warburton, *et al.* Nature **405**, 926 (2000).
- [17] J. J. Finley, *et al.* Phys. Rev. B **63**(16), 161305 (2001). doi:10.1103/PhysRevB.63.161305.
- [18] S. Raymond, *et al.* Phys. Rev. B **58**(20), R13415 (1998). doi:10.1103/PhysRevB.58.R13415.
- [19] J. A. Barker *et al.* Phys. Rev. B **61**(20), 13840 (2000). doi:10.1103/PhysRevB.61.13840.

- [20] J. J. Finley, *et al.* Phys. Rev. B **70**(20), 201308 (2004). doi:10.1103/PhysRevB.70.201308.
- [21] M. T. Borgström, *et al.* Nano Letters **5**(7), 1439 (2005). doi:10.1021/nl050802y.
- [22] D. Dalacu, *et al.* Nano Letters **12**(11), 5919 (2012). doi:10.1021/nl303327h.
- [23] J. Claudon, *et al.* Nature Photonics **4**, 174 (2010).
- [24] V. I. Klimov, editor. *Nanocrystal quantum dots*. CRC Press (2010).
- [25] J. Y. Marzin, *et al.* Phys. Rev. Lett. **73**, 716 (1994). doi:10.1103/PhysRevLett.73.716.
- [26] A. Berthelot, *et al.* Nat Phys **2**(11), 759 (2006). ISSN 1745-2473. doi:10.1038/nphys433.
- [27] P. Michler, *et al.* Science **290**, 2292 (2000).
- [28] M. Bayer, *et al.* Phys. Rev. B **65**(19), 195315 (2002). doi:10.1103/PhysRevB.65.195315.
- [29] G. Bester, *et al.* Phys. Rev. B **67**, 161306 (2003). doi:10.1103/PhysRevB.67.161306.
- [30] G. Bester *et al.* Phys. Rev. B **68**(7), 073309 (2003). doi:10.1103/PhysRevB.68.073309.
- [31] D. V. Regelman, *et al.* Phys. Rev. B **64**(16), 165301 (2001). doi:10.1103/PhysRevB.64.165301.
- [32] M. Ediger, *et al.* Nature Physics **3**, 774 (2007).
- [33] H. Drexler, *et al.* Phys. Rev. Lett. **73**, 224 (1994).
- [34] F. Findeis, *et al.* Phys. Rev. B **63**, 121309 (2001). doi:10.1103/PhysRevB.63.121309.
- [35] D. Loss *et al.* Phys. Rev. A **57**, 120 (1998).
- [36] M. V. G. Dutt, *et al.* Phys. Rev. Lett. **94**, 227403 (2005). doi:10.1103/PhysRevLett.94.227403.
- [37] D. Press, *et al.* Nature **456**, 218 (2008).
- [38] A. V. Khaetskii, *et al.* Phys. Rev. Lett. **88**, 186802 (2002). doi:10.1103/PhysRevLett.88.186802.
- [39] I. A. Merkulov, *et al.* Phys. Rev. B **65**(20), 205309 (2002). doi:10.1103/PhysRevB.65.205309.
- [40] B. Eble, *et al.* Phys. Rev. B **74**(8), 081306 (2006). doi:10.1103/PhysRevB.74.081306.
- [41] A. I. Tartakovskii, *et al.* Phys. Rev. Lett. **98**(2), 026806 (2007). doi:10.1103/PhysRevLett.98.026806.
- [42] P. Fallahi, *et al.* Phys. Rev. Lett. **105**, 257402 (2010). doi:10.1103/PhysRevLett.105.257402.
- [43] P. W. Fry, *et al.* Phys. Rev. Lett. **84**(4), 733 (2000). doi:10.1103/PhysRevLett.84.733.
- [44] T. Lundstrom, *et al.* Nature **286**, 2312 (1999).
- [45] M. Kroutvar, *et al.* Nature **432**, 81 (2004).
- [46] A. V. Khaetskii *et al.* Physical Review B **64**, 125316 (2001).
- [47] E. A. Stinaff, *et al.* Science **311**(5761), 636 (2006).
- [48] D. Kim, *et al.* Nature Phys. **7**, 223 (2011).

- [49] L. Robledo, *et al.* Science **320**(5877), 772 (2008). doi:10.1126/science.1155374.
- [50] A. A. Maksimov, *et al.* Phys. Rev. B **62**, R7767 (2000). doi:10.1103/PhysRevB.62.R7767.
- [51] J. A. Gaj *et al.*, editors. *Introduction to the Physics of Diluted Magnetic Semiconductors*. Springer-Verlag Berlin Heidelberg (2010).
- [52] L. Besombes, *et al.* Phys. Rev. Lett. **93**, 207403 (2004). doi:10.1103/PhysRevLett.93.207403.
- [53] C. Le Gall, *et al.* Phys. Rev. Lett. **102**(12), 127402 (2009). doi:10.1103/PhysRevLett.102.127402.
- [54] M. Goryca, *et al.* Phys. Rev. Lett. **103**(8), 087401 (2009). doi:10.1103/PhysRevLett.103.087401.
- [55] Y. Léger, *et al.* Phys. Rev. Lett. **97**(10), 107401 (2006). doi:10.1103/PhysRevLett.97.107401.
- [56] G. Bacher, *et al.* Phys. Rev. Lett. **89**, 127201 (2002). doi:10.1103/PhysRevLett.89.127201.
- [57] J. J. Zayhowski, *et al.* Phys. Rev. B **35**, 6950 (1987). doi:10.1103/PhysRevB.35.6950.
- [58] G. Mackh, *et al.* Phys. Rev. B **49**, 10248 (1994). doi:10.1103/PhysRevB.49.10248.
- [59] J. Seufert, *et al.* Phys. Rev. Lett. **88**, 027402 (2001). doi:10.1103/PhysRevLett.88.027402.
- [60] J. Fernández-Rossier *et al.* Phys. Rev. Lett. **93**(11), 117201 (2004).
- [61] S. Maćkowski, *et al.* App. Phys. Lett **84**, 3337 (2004). doi:10.1063/1.1723694.
- [62] A. Kudelski, *et al.* Phys. Rev. Lett. **99**(24), 247209 (2007). doi:10.1103/PhysRevLett.99.247209.
- [63] J. Kobak, *et al.* Nature Communications **5**, 3191 (2014).
- [64] Z. Wasilewski, *et al.* J. Cryst. Growth **201/202**, 1131 (1999).
- [65] J. Seufert, *et al.* Appl. Phys. Lett. **79**(7), 1033 (2001). doi:10.1063/1.1389504.
- [66] J. Seufert, *et al.* Appl. Phys. Lett. **82**(22), 3946 (2003). doi:10.1063/1.1580632.
- [67] S. Mackowski, *et al.* Phys. Rev. B **69**(20), 205325 (2004).
- [68] T. Kazimierczuk, *et al.* Phys. Rev. B **79**(15), 153301 (2009). doi:10.1103/PhysRevB.79.153301.
- [69] J. Suffczyński, *et al.* Phys. Rev. B **74**(8), 085319 (2006). doi:10.1103/PhysRevB.74.085319.
- [70] K. Kowalik, *et al.* phys. stat. sol. c **3**, 3890 (2006).
- [71] J. Bellessa, *et al.* Phys. Rev. B **58**(15), 9933 (1998).
- [72] F. Tinjod, *et al.* Journal of Applied Physics **95**(1), 102 (2004). doi:10.1063/1.1631755.
- [73] J. Kobak, *et al.* Acta Phys. Pol. A **119**(5), 627 (2011).
- [74] P. Hawrylak. Phys. Rev. B **60**, 5597 (1999). doi:10.1103/PhysRevB.60.5597.
- [75] R. Akimoto, *et al.* Phys. Rev. B **56**, 9726 (1997).

5 Description of other scientific achievements

5.1 Research done before obtaining the PhD title

5.1.1 Masters degree

I earned my Master's degree at the Department of Solid State Physics at the Faculty of Physics, University of Warsaw. I worked, under the supervision of prof. Andrzej Twardowski, on anomalies in the Zeeman splittings of excitonic transitions in semiconducting compounds doped with transition metal ions, i.e., the diluted magnetic semiconductors. These materials exhibit amplified magneto-optical effects, such as the Zeeman or Faraday effect, due to an exchange interaction between the band carriers and localized ions. This interaction is usually described in the framework of a mean field approximation (MFA) and a virtual crystal approximation (VCA). If the concentration of the transition metal ions is small, this description fails to correctly predict the Zeeman splitting. The discrepancy is due to a local potential that the dopants introduce to the crystal lattice. The aim of my work was to investigate the influence of this potential on the exciton Zeeman splitting in cadmium manganese telluride, $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$.

In this work, I conducted measurements of magnetization in a SQUID magnetometer and reflectivity in magnetic fields. The results allowed to assess the discrepancies between the observed splittings and those predicted by the above mentioned approximations. We obtained the dependence of the deviations from MFA and VCA as a function of the manganese concentration. The results were compared with calculations performed within two models taking into account the influence of the local potential introduced by the diluted ions. The results of these studies were published in the following papers:

- A1. **Ł. Kłopotowski**, M. Herbich, W. Mac, A. Stachow-Wójcik, and A. Twardowski *Influence of local potential on exciton splitting in highly diluted $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$* , Acta Physica Polonica A **92**, 837 (1997).
- A2. M. Herbich, **Ł. Kłopotowski**, W. Mac, A. Stachow-Wójcik, A. Twardowski, J. Tworzydło, M. Demianiuk *Influence of local potentials on spin splitting in diluted magnetic semiconductors*, Journal of Crystal Growth **184/185**, 992 (1998).

5.1.2 Ph.D. title

I worked on my PhD under the supervision of prof. Michał Nawrocki, also in the Department of Solid State Physics at the Faculty of Physics, University of Warsaw. The goal of my work was to evaluate the times of exciton tunneling between two coupled quantum wells and to provide answers to two questions: (i) does the tunneling process conserve spin and (ii) does the exciton tunnel as one entity or is it a two step process involving a separate tunneling of the electron and the hole. The motivation for this work was on the one hand the verification of existing theoretical models pointing out the role of phonons in the tunneling process and on the other hand the growing interest in spin effects in semiconductors related to the possible use of spin in novel, spintronic devices. The experimental tools we employed to provide answers to the above questions were reflectivity/transmission and photoluminescence measurements in magnetic fields. The former ones allowed to characterize the studied samples and determine the parameters crucial for the analysis of the tunneling efficiency, which was established with the use of either steady-state techniques such as the measurements of photoluminescence excitation spectra and the Hanle effect or time-resolved photoluminescence.

The results of the conducted research allowed us to conclude that during the exciton transfer between the wells the spin is indeed conserved. Furthermore, we showed that the tunneling efficiency depends crucially on the detuning between the initial and final state of the process. In particular, we proved that tunneling of excitons as single quasi-particles exhibits a resonant enhancement for detuning equal to twice the energy of longitudinal phonons.

During the course of these studies, I also investigated the impact of free carriers on the photoluminescence and absorption spectra of the quantum wells. The impact is manifested by the appearance of optical transitions due to charged excitons, so called trions. Quantitative analysis of the absorption spectra allowed to conclude that the non-equilibrium carriers are electrons. Photoluminescence studies showed that these carriers appear as a result of trapping of the photoexcited holes by surface states.

The results obtained within my Ph.D. studies were published in the following papers:

- B1. **Ł. Kłopotowski**, M. Nawrocki, J. A. Gaj, S. Maćkowski, E. Janik *Tunneling of spin polarized excitons in CdTe based asymmetric double quantum well structure*, Solid State Communications **119**, 147 (2001).
- B2. **Ł. Kłopotowski**, M. Nawrocki, S. Maćkowski, E. Janik *Spin conserving tunneling in asymmetric double quantum well structures*, physica status solidi b **229**, 769 (2002).
- B3. **Ł. Kłopotowski**, J. Suffczyński, S. Maćkowski, E. Janik *Exciton and charged exciton absorption in asymmetric double quantum well structures*, physica status solidi a **190**, 793 (2002).
- B4. **Ł. Kłopotowski**, J. Suffczyński, M. Nawrocki, E. Janik *Hanle effect of charged and neutral excitons in quantum wells*, Journal of Superconductivity **16**, 435 (2003).
- B5. M. Nawrocki, **Ł. Kłopotowski**, J. Suffczyński, *Optical spin injection and tunneling in asymmetric coupled II-VI quantum wells*, physica status solidi b **241**, 680 (2004).

5.2 Research done after obtaining the Ph.D. title: works not related to the topic of the thesis

5.2.1 Photoluminescence dynamics of exciton polaritons

After completing the Ph.D., I left for a post-doc to Universidad Autónoma de Madrid, where I joined the group of prof. Luis Viña. During my 18 month stay, I studied the properties of quasiparticles which appear as a result of a strong coupling of light and matter or, in other words, the exciton in a quantum well and a electromagnetic field mode of a planar microcavity. These quasiparticles are known as exciton polaritons. They keep attracting the interest of the scientific community from the aspects of both the fundamental studies and possible applications. The combination of exciton and photon properties hold promise for applications as novel, energy efficient light sources. Also, the bosonic nature of exciton polaritons allows to investigate such effects as Bose-Einstein condensation and superfluidity in purely solid state environments. My work concentrated on two aspects of dynamical properties of polaritons. I studied the influence on the photoluminescence dynamics of the basic parameters that characterize the light-matter coupling: the energy detuning between the quantum well exciton and the cavity mode, polariton density, and polariton wave vector k_{\parallel} . Moreover, I wanted to understand what mechanisms determine the polarization of the emitted light, the dynamics of this polarization and, in particular, the polariton spin relaxation.

Within the course of this research, we showed that there are three regimes of the polariton density, in which different mechanisms control the photoluminescence and spin dynamics. In the linear regime, the photoluminescence decay is relatively slow (occurring on a timescale of ~ 100 ps) and the energy relaxation toward the ground state at $k_{\parallel} = 0$ takes place via polariton-polariton scattering. The photoluminescence polarization can be imprinted by optical orientation of the photoexcited carriers. At higher densities, the relaxation toward the ground state is importantly accelerated by scattering stimulated by final state population, a purely bosonic effect. The photoluminescence lifetimes shortens to few tens of ps. In this regime of stimulated scattering, polarization oscillations are observed resulting from a splitting between the TE and TM

cavity modes. Further increase of the polariton density results in screening of the electron-hole Coulomb interaction and decreasing of the exciton-photon coupling, which ultimately vanishes at the onset of the saturation regime. Thereupon, the photoluminescence is dominated by the lasing from an electron-hole plasma. Our studies of photoluminescence dynamics showed that indeed in time after photoexcitation, with emptying of the cavity and decreasing of the carrier density, a transition from the saturation to the stimulated scattering to the linear regime may occur.

Investigations of the linear polarization of the photoluminescence proved a presence of a strong anisotropy of the polariton optical properties. We observed a degree of linear polarization reaching 100% in the stimulated emission. The analysis of this polarization showed that it did not originate from a crystallographic anisotropy, i.e., the lack of mirror symmetry between the two quantum well interfaces. This effect strongly influences the properties of quantum well excitons, but for polaritons with a small excitonic content it is of minor importance. We demonstrated that the dominant mechanism responsible for the observed anisotropy is a small birefringence of the Bragg mirrors of the cavity. The birefringence is probably due to a uniaxial strain present in the cavity plane.

- C1. **Ł. Kłopotowski**, L. Viña, Le Si Dang, R. André, *Time-Resolved Emission from Semiconductor Microcavities*, Acta Physica Polonica **106**, 435 (2004).
- C2. **Ł. Kłopotowski**, R. Santos, A. Amo, M. D. Martín, L. Viña, R. André, *Dynamics of Polariton Emission in the Linear Regime*, Acta Physica Polonica **106**, 443 (2004).
- C3. **Ł. Kłopotowski**, A. Amo, M. D. Martín, L. Viña, R. André, *Polarization Dynamics of Microcavity Polaritons: Three Excitation Regimes*, physica status solidi (a) **202**, 357 (2005).
- C4. **Ł. Kłopotowski**, M. D. Martín, A. Amo, L. Viña, I. A. Shelykh, M. M. Glazman, G. Malpuech, A. V. Kavokin, R. André, *Optical Anisotropy and Pinning of the Linear Polarization of Light in Semiconductor Microcavities*, Solid State Communications **139**, 511 (2006).

5.2.2 Optical properties of zinc oxide layers and nanostructures

After returning from the post-doc, I joined the group of prof. Grzegorz Karczewski at the Institute of Physics, Polish Academy of Sciences as an adjunct. The first subject I worked on was related to the possibility of doping zinc oxide with transition metal ions, to develop a wide band gap diluted magnetic semiconductor.

Zinc oxide is a semiconducting compound which can be synthesized via numerous procedures ranging from oxidation of organic precursors to molecular beam epitaxy. Many of these methods are facile and cheap, which makes ZnO interesting for researchers focused on device applications. Direct band gap in the near ultraviolet range and a large exciton binding energy of about 70 meV suggest many applications of ZnO in optoelectronics. Crucially, theoretical models predict that ZnO doped with transition metal ions (manganese in particular) should exhibit ferromagnetism in room temperature provided that a significantly high concentration of holes is present. At the moment when we were undertaking these studies, developing ferromagnetic semiconductors remained an important goal for spintronics and, thus, reports on *p*-doping and manganese doping of ZnO attracted a lot of attention.

Upon joining the team at the Institute of Physics, I started working with Ewa Przeździecka, the Ph.D. student of prof. Jacek Kossut, on optical properties of ZnO fabricated by oxidation of epitaxially grown ZnTe. This method was applied because of the well developed technique of the *p*-type doping of ZnTe by nitrogen plasma.

In the article Z1, we studied the exciton Zeeman splitting in a p -doped ZnMnO alloy. My role in these studies was related to assisting with conducting and interpreting the photoluminescence measurements in magnetic fields. We observed a splitting increased with respect to pure ZnO, which proved that a semimagnetic compound was indeed fabricated. It also allowed to estimate the exchange constants.

In Z2, we studied different strategies for p -type doping of the ZnO layers. We showed that in fact doping with nitrogen is less efficient than doping with arsenic acceptors, which are incorporated into ZnO as a result of diffusion from the GaAs substrate occurring during annealing. In the photoluminescence spectra, we identified transitions related to excitons bound on different acceptors, which was an important element for the interpretation of the transport results. My role in these experiments was also related to the help with conducting the photoluminescence studies and interpreting the results.

Apart from the MBE growth and subsequent oxidation of ZnTe epi-layers, we also developed techniques, which allowed to fabricate ZnO nanostructures. Articles Z3 and Z4 are devoted, respectively, to studies of ZnO tetrapods and nanowires grown by, respectively, low pressure vapour phase synthesis and a carbo-thermal method. With the use of these techniques monocrystal nanoobjects can be fabricated. The nanowires exhibit lengths of up to 10 microns and diameters of about 100 nm. The forms of tetrapods on the other hand depend on the growth temperature. Both techniques provide samples with intense photoluminescence, visible at room temperature. My role in these studies was assistance with the photoluminescence measurements and interpretation of the results and writing of the manuscripts.

Another technique that we applied to fabricate ZnO nanostructures was electrospinning. In this method, a polymer solution containing zinc acetate is shaped into a thread, which can be deposited on various substrates by application of an electric potential. Under calcination, zinc acetate oxidizes to form ZnO in the shape of nanofibers, which contain crystallites with diameters ranging from a few to about 100 nm, depending on the calcination temperature. Large surface to volume ratio of the crystallites together with the feasibility of deposition of the nanofibers on different substrates are the characteristics, which give hope to develop nanosensors based on the electrospun material. The aim of the studies in which I took part, was to investigate optical properties of the ZnO nanofibers and, in particular, its sensitivity to the environment. The results were published in Z5, Z6, and Z7. In these works, we presented a thorough morphological characterization as well as the studies of photoluminescence and sensoric properties. My input into these studies was conducting the photoluminescence experiments and setting up the studies of photosensitivity dynamics. I also took part in interpreting the experimental data and writing of the manuscripts. In particular, in these articles we demonstrated the influence of molecular oxygen absorption on the conductivity of the nanofibers (Z5). We also showed the possibility to develop biocompatible magnetic nanofibers by doping ZnO with iron (Z6). Moreover, we demonstrated how to increase the conductance and environmental sensitivity of the nanofibers by proper passivation of the surface states (Z7).

- Z1. E. Przeździecka, E. Kamińska, M. Kiecana, M. Sawicki, **Ł. Kłopotowski**, W. Pacuski, and J. Kossut, *Magneto-optical properties of the diluted magnetic semiconductor p -type ZnMnO*, Solid State Communications **139**, 541 (2006).
- Z2. E. Przeździecka, E. Kamińska, K. P. Korona, E. Dynowska, W. Dobrowolski, R. Jakiela, **Ł. Kłopotowski**, and J. Kossut, *Photoluminescence Study and Structural Characterization of p -type ZnO doped by N and/or As acceptors*, Semiconductor Science and Technology **22**, 10 (2007).
- Z3. W. Zaleszczyk, K. Fronc, M. Aleszkiewicz, W. Paszkowicz, J. Wróbel, P. Dłużewski, S. Kret, M. Klepka, **Ł. Kłopotowski**, G. Karczewski and T. Wojtowicz, *Photoluminescence Properties of ZnO and ZnCdO Nanowires*, Acta Physica Polonica **112**, 357 (2007).

- Z4. W. Zaleszczyk, K. Fronc, E. Przeździecka, E. Janik, M. Czapkiewicz, J. Wróbel, W. Paszkowicz, **Ł. Kłopotowski**, G. Karczewski, T. Wojtowicz, and A. Presz *Photoluminescence Properties of ZnO Nanowires Grown on Ni Substrate*, *Acta Physica Polonica* **114**, 1451 (2008).
- Z5. A. Baranowska-Korczyc, K. Fronc, **Ł. Kłopotowski**, A. Reszka, K. Sobczak, W. Paszkowicz, K. Dybko, P. Dłużewski, B. J. Kowalski, D. Elbaum, *Light- and environment-sensitive electrospun ZnO nanofibers*, *RSC Advances* **3**, 5656 (2013).
- Z6. A. Baranowska-Korczyc, A. Reszka, K. Sobczak, B. Sikora, P. Dziawa, M. Aleszkiewicz, **Ł. Kłopotowski**, W. Paszkowicz, P. Dłużewski, B. J. Kowalski, T. A. Kowalewski, M. Sawicki, D. Elbaum, K. Fronc, *Magnetic Fe doped ZnO nanofibers obtained by electrospinning*, *Journal of Sol-Gel Science and Technology* **61**, 494 (2012).
- Z7. A. Baranowska-Korczyc, K. Sobczak, P. Dłużewski, A. Reszka, B. J. Kowalski, **Ł. Kłopotowski**, D. Elbaum, K. Fronc, *Facile synthesis of core/shell ZnO/ZnS nanofibers by electrospinning and gas-phase sulfidation for biosensor applications*, *Physical Chemistry Chemical Physics* **17**, 24029 (2015).
- Z8. J. Mikulski, B. Sikora, K. Fronc, P. Aleshkevych, S. Kret, J. Suffczyński, J. Papierska, **Ł. Kłopotowski**, and J. Kossut, *Synthesis and magnetooptic characterization of Cu-doped ZnO/MgO and ZnO/oleic acid core/shell nanoparticles*, *RSC Advances* **6**, 44820 (2016).

5.2.3 Zinc telluride nanowires

Nanowires are nanostructures characterized by a large length to diameter ratio. Although they are considered as one-dimensional structures, usually their diameter is significantly larger than exciton Bohr radius and the density of states is the same as for bulk materials. As a consequence, the optical properties of nanowires usually do not exhibit any characteristics of low dimensional structures. However, the strong shape anisotropy and the large surface-to-volume ratio make nanowires promising building blocks for future photonic or sensoric applications. Additional consequence of the shape anisotropy, which distinguishes nanowire heterostructures from planar ones, is the possibility to combine materials with larger lattice mismatch before defects develop. In the planar growth, lattice mismatch results in strain, which leads to appearance of dislocations. These defects constitute nonradiative recombination centers and deteriorate the optical quality of heterostructures. Combining lattice mismatched materials in nanowires allows to sustain much larger strains before the dislocations are formed.

The studies on nanowires in which I took part were conducted with Piotr Wojnar (another adjunct in our group) and Małgorzata Szymura, who is a Ph.D. student of prof. Jacek Kossut with me as an auxiliary supervisor. These studies were concerned with photoluminescence properties of ZnTe nanowires and also CdTe quantum dots embedded into such nanowires. The motivation for this work was a possible application of these heterostructures in optoelectronic devices operating in the so-called yellow spectral region. My input into the articles D1 and D2 was conducting measurements of linear polarization anisotropy of the photoluminescence of single nanowires. These studies constituted an important part of optical characterization of these nanostructures. Due to presence of the surface states acting as non-radiative recombination centers, uncoated (core-only) ZnTe nanowires do not emit light. The growth of a radial, core-shell heterostructure by overgrowing the ZnTe core with a semiconductor with a larger bandgap leads to passivation of the surface states and activation of the photoluminescence. The aim of the studies published in article D3 was to quantitatively describe the impact of the shell thickness on the nanowire photoluminescence. We performed time-resolved photoluminescence measurements on nanowire ensembles and single heterostructures and showed that the photoluminescence lifetime and intensity both increase with the shell thickness. These processes are controlled by

tunneling of electrons to the surface states. The shell constitutes the tunnel barrier and thus its thickness controls the efficiency of this process. A phenomenological model based on the WKB approximation allowed to reproduce the observed photoluminescence decays and also propose strategies for improving the light emission efficiency. Studies of single nanowires revealed that under a strong excitation pulse, the carrier density is large enough to screen completely the Coulomb interaction. As a result, electron-hole plasma develops and is responsible for the photoluminescence shortly after the excitation pulse. Moreover, the many body interactions present in this regime lead to renormalization of the nanowire band gap. I conceived the experiments for D3 and supervised the measurements. I also proposed the theoretical model allowing for the quantitative description of the experimental data and wrote most of the manuscript.

I was also involved in the studies of radial heterostructures: CdTe quantum dots grown in ZnTe nanowires. The growth of such quantum dots does not rely on the relaxation of strain as in the Stranski-Krastanow mechanism. The dot is grown as a radial insertion into the one dimensional wire. Moreover, the growth occurs along a different crystallographic direction than in the planar structures. Therefore, one might expect different optical properties of the nanowire and Stranski-Krastanow quantum dots. The aim of D4 was to identify the ground state of the exciton confined in such a nanowire quantum dot. Theoretical works suggest that under specific growth conditions the light hole exciton may lie lower in energy, opposite to the case of Stranski-Krastanow dots, where universally the ground state is the heavy hole exciton. For this task, we applied a novel experimental tool. Namely, we investigated the Zeeman splitting of the photoluminescence for magnetic fields which could be applied along an arbitrary angle to the nanowire axis. We observed that the splitting for the field oriented along the nanowire axis is a few times larger than for the perpendicular orientation. Comparing these results with calculations we concluded that for the investigated nanowires the ground state is indeed the heavy hole exciton. The calculations allowed also to evaluate the degree of heavy-light hole mixing in the ground state. The article D4 consists of two parts. The first one is devoted to the studies of axial heterostructures, i.e., core-shell nanowires. In the second one, studies on radial heterostructures are presented, i.e. on quantum dots. My input was mainly into the second part. I assisted in the photoluminescence measurements, supervised the data analysis, proposed the model describing the Zeeman splitting anisotropy, and took part in writing of the manuscript.

We also undertook studies on identification of the photoluminescence transitions in the spectra of single nanowires containing quantum dots. The initial identification was based on the behavior of the lines with as a function of the excitation power. This method allowed to identify some of the transitions and also demonstrate the photoluminescence from higher shells. The results were published in D5. My input into this work was conceiving the experiments, help with performing them, supervising the data analysis and help with writing the manuscript.

- D1. P. Wojnar, M. Szymura, W. Zaleszczyk, **Ł. Kłopotowski**, E. Janik, M. Wiater, L. T. Baczewski, S Kret, G. Karczewski, J. Kossut and T. Wojtowicz, *Activation of an intense near band edge emission from ZnTe/ZnMgTe core/shell nanowires grown on silicon*, Nanotechnology **24**, 365201 (2013).
- D2. P. Wojnar, M. Zieliński, E. Janik, W. Zaleszczyk, T. Wojciechowski, R. Wojnar, M. Szymura, **Ł. Kłopotowski**, L. T. Baczewski, A. Pietruchik, M. Wiater, S Kret, G. Karczewski, T. Wojtowicz and J. Kossut, *Strain-induced energy gap variation in ZnTe/ZnMgTe core/shell nanowires*, Applied Physics Letters **104**, 163111 (2014).
- D3. M. Szymura, **Ł. Kłopotowski**, A. A. Mitioglu, P. Wojnar, G. Karczewski, T. Wojtowicz, D. K. Maude, P. Płochocka, and J. Kossut , *Exciton and carrier dynamics in ZnTe-Zn_{1-x}MgxTe core-shell nanowires*, Physical Review B **93**, 155429 (2016).
- D4. M. Szymura, P. Wojnar, **Ł. Kłopotowski**, J. Suffczyński, M. Goryca, T. Smoleński, P. Kossacki, W. Zaleszczyk, T. Wojciechowski, G. Karczewski, T. Wojtowicz and J. Kos-

sut, *Spin Splitting Anisotropy in Single Diluted Magnetic Nanowire Heterostructures*, Nano Letters **15**, 1972 (2015).

- D5. M. Szymura, **Ł. Kłopotowski**, P. Wojnar, G. Karczewski, T. Wojtowicz and J. Kossut, *Identification of Optical Transitions from CdTe and CdMnTe Quantum Dots Embedded in ZnTe Nanowires*, Acta Physica Polonica **124**, 824 (2013).

5.2.4 Excitons in two dimensional semiconductors

After completing the research projects related to CdTe quantum dots, I became interested in properties of two dimensional semiconductors. The materials belonging to this family are characterized by atomically thin layers, weakly bound together by van der Waals forces, which enables to obtain monolayers by mechanical cleavage. Being a spectroscopist, I am mostly interested in materials with a direct band gap, such as transition metal dichalcogenides. These compounds in their bulk form exhibit an indirect gap, but upon thinning down to a monolayer, the gap becomes direct, located at the inequivalent $\pm K$ corners of the hexagonal Brillouin zone. Thus, the $\pm K$ valleys can be treated as a binary index, a pseudospin. Monolayer thickness is about 7 Å and thus dielectric screening is weak, which leads to very strong excitonic effects. Indeed, the exciton binding energies reach hundreds of meV and are one or two orders of magnitude larger than in conventional semiconductors or their nanostructures. From the point of view of optical selection rules, it is important to note that the monolayer lacks inversion symmetry. Thus, the orbital magnetic moment related to the self-rotation of the Bloch electron wave function has opposite sign in $+K$ and $-K$ valleys. As a consequence, optical transitions in σ^\pm polarizations involve carriers in $\pm K$ valleys, allowing to selectively address the valley pseudospin, much like the electron spin can be oriented with circularly polarized light in conventional semiconductors. Recently, manipulating the valley pseudospin is actively sought in view of applications in novel *valleytronic* devices.

The studies of valley effects in transition metal dichalcogenides I perform in collaboration with Laboratoire National de Champs Magnétique Intenses — Toulouse. Spectroscopy in high magnetic fields allows to understand the nature of electronic states. The exciton Zeeman splitting usually scales with a Landé factor $g = -4$. In the article P1, we investigated exciton Zeeman splittings in MoS₂ and MoSe₂ showed deviations from $g = -4$. We discussed the possible influence of strain on the magnitude of the Zeeman splittings. My contribution to this work was the help in interpreting the data and writing of the manuscript. MoS₂ and MoSe₂ monolayers studied in P1 were grown by chemical vapour deposition. An alternative technique, and one scalable for applications, is liquid phase exfoliation, where the monolayers are obtained by sonication or shearing of bulk powder in a properly chosen liquid. I investigated optical properties of liquid exfoliated WS₂ monolayers. In article P2 I showed that excitons in these nanosheets are bound to defects, most probably localized on nanosheet edges. These excitons share some properties with quantum dots, e.g., exhibit a strong sensitivity to environment. Moreover, the Zeeman splittings are larger because the optical transitions are not restricted to the band edges. Indeed, for these localized states the valley pseudospin is not a good quantum number. Nevertheless, the photoluminescence of the liquid exfoliated WS₂ reveals a strong circular dichroism, inherited from the valley polarized free excitons. For P2, I performed the measurements, analyzed and interpreted the data, and wrote the manuscript with the help of the co-authors.

I also took part in studies of another member of two dimensional semiconductor family — monolayer black phosphorus (sometimes, in analogy to graphene, named phosphorene). In the article P3 we studied the influence of excitation density on photoluminescence dynamics and showed that in phosphorene it is possible to attain much larger exciton densities than in transition metal dichalcogenides. The limiting effect is exciton-exciton annihilation, excitonic analog of the Auger effect. We showed that in phosphorene the efficiency of this process is 1-2 orders of magnitude smaller than in other two dimensional semiconductors. My contribution to

this work was to propose a method for and take part in data analysis and help with writing the manuscript.

- P1. A. A. Mitiglu, K. Galkowski, A. Surrente, **Ł. Kłopotowski**, D. Dumcenco, A. Kis, D. K. Maude, and P. Plochocka, *Magnetoexcitons in large area CVD-grown monolayer MoS₂ and MoSe₂ on sapphire*, Physical Review B **93**, 165412 (2016).
- P2. **Ł. Kłopotowski**, C. Backes, A. A. Mitiglu, V. Vega-Mayoral, D. Hanlon, J. N. Coleman, V. Y. Ivanov, D. K. Maude, and P. Plochocka, *Revealing the nature of excitons in liquid exfoliated monolayer tungsten disulphide*, Nanotechnology **27**, 425701 (2016).
- P3. A. Surrente, A. A. Mitiglu, K. Galkowski, **Ł. Kłopotowski**, W. Tabis, B. Vignolle, D. K. Maude, and P. Plochocka, *Onset of exciton-exciton annihilation in single-layer black phosphorus*, Physical Review B **94**, 075425 (2016).

5.3 Research done after obtaining the Ph.D. title: works related to the topic of the thesis

The projects described below also deal with optical properties of CdTe quantum dots. The studies were conducted in collaboration with the group of Piotr Kossacki from the Faculty of Physics, Warsaw University. They are not included in this thesis as I cannot claim to have had a leading role.

Articles Q2, Q3, and Q4 deal with different influences of carrier-carrier exchange interactions on the fine structure of photoluminescence transitions. In Q2, we analyzed the impact of electron-hole exchange on the spectra of the negatively charged biexciton X^{2-} and doubly charged exciton X^{2-} . We showed how this interaction competes with the Zeeman effect. It is important to remark in view of the main achievement reported in the present thesis that the article Q2 confirmed the universality of the transition sequence for different excitonic species in CdTe quantum dots, first reported in H3. This conclusion was strengthened by analyzing about 100 quantum dots. My contribution to Q2 was the assistance in measurements of the transition sequences, in data analysis, and writing of the manuscript.

Electron-hole exchange removes the degeneracy of bright and dark neutral exciton states. The dark state has a lower energy, it cannot recombine radiative, but its population may decay by a spin-flip of one of the carriers and thus a conversion to a bright state. In article Q3 we showed that another mechanism is possible and in fact dominates the decay of the dark excitons in CdTe quantum dots. Namely, the mixing between heavy- and light-hole states enables a radiative recombination of such a mixed "dark" exciton. Photon emission takes place along the direction perpendicular to the growth axis, i.e., from the sample edge. My contribution to Q3 was the assistance in the photoluminescence measurements, discussion of the results, and writing of the manuscript.

I also took part in experiments aimed at imaging of optical modes of a photonic microcavity containing CdTe quantum dots. These results were published in Q1.

- Q1. T. Jakubczyk, T. Kazimierczuk, A. Golnik, P. Bienias, W. Pacuski, C. Kruse, D. Hommel, **Ł. Kłopotowski**, T. Wojtowicz, J. A. Gaj, *Optical Study of ZnTe-Based 2D and 0D Photonic Structures Containing CdTe/ZnTe Quantum Dot*, Acta Physica Polonica A **116**, 888 (2009).
- Q2. T. Kazimierczuk, T. Smolenski, M. Goryca, **Ł. Kłopotowski**, P. Wojnar, K. Fronc, A. Golnik, M. Nawrocki, J. A. Gaj, P. Kossacki, *Magnetophotoluminescence study of intershell exchange interaction in CdTe/ZnTe quantum dots*, Physical Review B **84**, 165319 (2011).
- Q3. T. Smoleński, T. Kazimierczuk, M. Goryca, M. Jakubczyk, **Ł. Kłopotowski**, L. Cywinski, P. Wojnar, A. Golnik, P. Kossacki, *In-plane radiative recombination channel of a dark exciton in self-assembled quantum dots*, Physical Review B **86**, 241305 (2012).

- Q4. T. Kazimierzuk, T. Smoleński, J. Kobak, M. Goryca, W. Pacuski, A. Golnik, K. Fronc, **Ł. Kłopotowski**, P. Wojnar, P. Kossacki, *Optical study of electron-electron exchange interaction in CdTe/ZnTe quantum dots*, Physical Review B **87**, 195302 (2013).

5.4 Participation in research projects

As a principal investigator:

- 2000: Grant from the Committee for Scientific Research no. 2 P03B 157 18 *Tunneling of excitons in asymmetric double quantum well structures*
- 2008 — 2009: POLONIUM Programme of the Ministry of Science and Higher Education
- 2007 — 2010: Grant from the Ministry of Science and Higher Education no. N N202 0634 33 *Elektryczne sterowanie stanem spinowym kropek kwantowych z CdTe domieszkowanych manganem*
- 2011 — 2014: Grant OPUS from Polish National Science Center (NCN) no. 2011/01/B/ST3/02287 *Magnetic quantum dot molecules with CdMnTe quantum dots*
- 2016 — 2018: Grant PICS (according to a bilateral agreement PAN — CNRS) *Spin and pseudospin relaxation in two dimensional semiconductors*

As an investigator:

- 2002 — 2003: Ph.D. grant from the Committee for Scientific Research no. 2 P03B 111 22 *Magneto-optical studies of exciton tunneling in asymmetric double quantum well structure*
- 2002: Grant from the Committee for Scientific Research no. PBZ-KBN-044/P03/2001 *Spin electronics - optical studies of spin correlations*
- 2004 — 2005: 6th Framework Programme grant *Novel Scalable Memory Concepts and Technologies*
- 2014 — 2016: Grant Sonata 1 from Polish National Science Center (NCN) no. 2011/01/D/ST5/05039 *Growth of optically active radial and axial nanowire heterostructures*
- 2014 — present: Grant Maestro 4 from Polish National Science Center (NCN) no. 2013/08/A/ST3/00297 *Semimagnetic quantum dot doped with copper*

5.5 Conference talks

1. 2016: Carbon Nanotubes meet 2D materials 2016, Heidelberg, Germany — *Spin-valley dynamics in monolayer transition metal dichalcogenides* — invited talk
2. 2016: 33rd International Conference on the Physics of Semiconductors, Beijing, China, *Intervalley exciton relaxation in monolayer tungsten diselenide under strong excitation*
3. 2016: NanoTech Poland, Poznań, *Excitons in two dimensions — optical properties of liquid exfoliated monolayer WS₂* — invited talk
4. 2016: 45th International School and Conference on the Physics of Semiconductors, Jas-zowiec, Wisła, Poland, *Inter-valley exciton relaxation in strongly excited monolayer WSe₂*
5. 2014: 32nd International Conference on the Physics of Semiconductors, Austin, USA, *Electronic Coupling in Double CdTe Quantum Dots*

6. 2011: 40th International School and Conference on the Physics of Semiconductors, Jaszowiec, Wisła, Poland, *Charging effects in self-assembled CdTe quantum dots* — invited talk
7. 2011: 15th International Conference on II-VI Compounds Cancún, Mexico, *Charge Control and Storage in Self-Assembled CdTe Quantum Dots*
8. 2011: Congree of Polish Physicists, Lublin, *Spontaneous magnetization in semiconductor quantum dots*
9. 2011: Symposium of Polish and Russian Academies of Science, Warsaw, Poland, *Charging Effects in Self-Assembled CdTe Quantum Dots*
10. 2011: Meeting of National Laboratory for Quantum Technologies, Warsaw, Poland, *Optical formation of magnetization in CdMnTe quantum dots*
11. 2010: Canada – France Symposium, Ottawa, Canada, *Towards Electrically Controlled Magnetization in Single CdMnTe Quantum Dots* — invited talk
12. 2010: 30th International Conference on the Physics of Semiconductors, Seoul, South Korea, *Formation Dynamics of Spontaneous Magnetization in Single Self-assembled CdMnTe Quantum Dots*
13. 2010: 39th International School and Conference on the Physics of Semiconductors, Jaszowiec, Wisła, Poland, *Formation Dynamics of Magnetic Polarons in Single Self-assembled CdMnTe Quantum Dots*
14. 2009: Candian – Japanese – Polish Symposium, Wrocław, Poland, *Coulomb Interactions and Charge Storage in CdTe Quantum Dots* — invited talk
15. 2009: 3rd National Nanotechnology Conference, Warsaw, Poland, *Quantum dots in electric fields* — invited talk
16. 2008: Optics of Nanostructures, Toruń, Poland, *Photoluminescence Spectroscopy of Single Self-assembled CdTe Quantum Dots in Electric Fields*
17. 2008: 29th International Conference on the Physics of Semiconductors, Rio de Janeiro, Brasil, *Quantum Confined Stark Effect in Single Self-assembled CdTe Quantum Dots*
18. 2007: International Workshop on Quantum Dot Lasers and Applications, Wrocław, Poland, *Optical and electrical charging of self assembled CdTe quantum dots*
19. 2006: 35th International School and Conference on the Physics of Semiconductors, Jaszowiec, Poland, *Spatial Mapping of the Probability Densities of Carriers Confined in Rectangular Quantum Wells*
20. 2004: Physics of Light-Matter Coupling in Nitrides 4, Sankt-Petersburg, Russia, *Polarization dynamics of microcavity polaritons: Three excitation regimes*
21. 2004: 27th International Conference on the Physics of Semiconductors, Flagstaff, USA, *Polarization of Light Emission in Semiconductor Microcavities: Dispersion Mapping*
22. 2003: Quantum State Engineering and Ultrafast Optical Interactions in Semiconductors, Toledo, Spain, *Intra- and Interwell Spin Relaxation In an Asymmetric Double Quantum Well System*
23. 2003: International Conference on Hot Carriers in Semiconductors, Modena, Italy, *Tunneling of Spin Polarized Holes In Asymmetric Double Quantum Well System*

24. 2002: Mini-Symposium on Optical Orientation and Spintronics, Lake District, Great Britain, *Hanle Effect of Quantum Well Excitons*
25. 2001: 10th International Conference on II-VI Compounds, Bremen, Germany, *Spin Conserving Tunneling In Asymmetric Double Quantum Well Structures*
26. 2001: High Magnetic Field Network Annual Meeting, Nijmegen, Holland,
27. 2001: 30th International School and Conference on the Physics of Semiconductors, Jas-zowiec, Poland, *Exciton Spin and Energy Relaxation Studies in Asymmetric Double Quantum Well Structure*

5.6 Collaborations with international and Polish institutions

- University of Warsaw, Faculty of Physics — collaboration with the group of prof. M. Nawrocki i prof. P. Kossacki on magnetospectroscopy on charging effects in single quantum dots. Results of this collaboration are published in H1, H2, H6 i H9, and Q1, Q2, Q3, and Q4.
- University of Sheffield, Great Britain — collaboration with the group of prof. M. S. Skolnick i A. I. Tartakovkii on Stark spectroscopy of single CdTe quantum dots in Schottky diode structures. Results of this collaboration are published in H4 i H5.
- Laboratoire de Photonique et Nanostructures, CNRS, Marcoussis, France — collaboration with the group of prof. O. Krebs on fabrication and characterization of Schottky diodes embedding quantum dots. Results of this collaboration are published in H4 i H5.
- Institut de NanoScience de Paris, Universite Pierre et Marie Curie, CNRS, Francja — collaboration with the group of V. Voliotis on photoluminescence dynamics of single quantum dots. Results of this collaboration are published in H2, H3, H4 i H5.
- The University of Rzeszów, Faculty of Mathematics and Natural Sciences — collaboration with prof. M. Parlińska-Wojtan (now at AGH University of Science and Technology) on structural characterization by transmission electron microscopy of samples containing double quantum dots. Results of this collaboration are published in H8.
- Laboratoire National de Champs Magnétique Intenses — Toulouse — collaboration with the group of P. Plochocka and D. K. Maude on valley effects and photoluminescence dynamics in two dimensional semiconductors. Results of this collaboration are published in P1, P2, and P3.

5.7 Research visits

- 2016: Laboratoire National de Champs Magnétique Intenses, Toulouse, France — Transient absorption studies on monolayer MoSe₂ grown by chemical vapour deposition
- 2015: Laboratoire National de Champs Magnétique Intenses, Toulouse, France — Valley polarization in liquid exfoliated monolayer WS₂
- 2010: Laboratoire National de Champs Magnétique Intenses, Grenoble, France — Magnetophotoluminescence study of CdMnTe quantum dots embedded in *p-i-n* diodes.
- 2008 — 2010: Institut de NanoScience de Paris, Université Pierre et Marie Curie, CNRS, France — Three visits of couple of weeks each. Formation dynamics of spontaneous magnetization in CdMnTe quantum dots.

- 2007 — 2008: Department of Physics and Astronomy, University of Sheffield, Great Britain — Two visits of couple of weeks each. Measurement of quantum confined Stark effect in CdTe quantum dots.
- 2006: Laboratoire de Photonique et Nanostructures, CNRS, Marcoussis, France — Fabrication of Schottky diodes containing CdTe quantum dots.
- 2003 — 2004: Universidad Autónoma de Madrid, Spain — Post-doctoral stay. Dispersion mapping and photoluminescence dynamics of exciton polaritons.
- 2002: École Polytechnique Fédéral de Lausanne, Switzerland — Exciton tunneling dynamics in asymmetric double quantum wells.
- 2001: Universidad Autónoma de Madrid, Spain — Time-resolved photoluminescence studies by *up-conversion*.
- 1999: Université Montpellier II, France — Time-resolved photoluminescence studies with a streak camera.

5.8 Awards

- 2003: National Fellowship for Young Researchers START, Foundation for Polish Science
- 2001: Young Authors' Award on 10th International Conference on II-VI Compounds, Bremen, Germany

6 Other activities

6.1 Teaching

- 2011 — now: Institute of Physics, Polish Academy of Sciences — supervising the Ph.D. of Małgorzata Szymura (auxiliary supervisor)
- 2012 — 2016: Institute of Physics, Polish Academy of Sciences — co-teaching Laboratory *New materials: technology and design* for II/III year students of Nanostructure Engineering Faculty of Chemistry/Faculty of Physics, University of Warsaw. Four semesters.
- 2013 — 2014: Institute of Physics, Polish Academy of Sciences — supervising summer practices for Faculty of Physics, University of Warsaw. Two persons.
- 2010 — 2011: Cardinal Wyszyński University — supervising Masters degree of Małgorzata Szymura *Spectroscopy of single CdMnTe quantum dots*.
- 2012: Institute of Physics, Polish Academy of Sciences — Lecture for students of Department of Mechatronics, Warsaw University of Technology on non-classical light sources.
- 2011: Institute of Physics, Polish Academy of Sciences — Lecture for students of Department of Mechatronics, Warsaw University on applications of quantum dots in future cryptography.
- 2010: Institute of Physics, Polish Academy of Sciences — Lecture for students of Department of Mechatronics, Warsaw University on quantum dots as single photon sources.
- 2008: Cardinal Wyszyński University — supervising Masters degree of Agnieszka Gruszczyńska *Wave function mapping in quantum wells using the Zeeman effect*.
- 2003: Universidad Autónoma de Madrid, Spain — Individual Masters Laboratory.

- 1997 — 2002: Faculty of Physics, University of Warsaw. Introductory physics for I and II year students. Five semesters. Introduction to atomic, molecular, and solid state physics. Two semesters.

6.2 Outreach

- 2016: Workshop for participants of the Polish Children's Fund *Quantum dots: how zero dimensional electron traps emit light*
- 2012: Workshop for participants of the Polish Children's Fund *Quantum dots: how zero dimensional electron traps emit light*
- 2011: Workshop for participants of the Polish Children's Fund *Quantum dots: how zero dimensional electron traps emit light*
- 2010: Workshop for participants of the Polish Children's Fund *Quantum Hall effect — electron transport through nanometer semiconductor layers and evaluation of the Planck's constant.*
- 2009: Workshop for participants of the Interdisciplinary Camp of of the Polish Children's Fund in Otwock *Singing sands or pattern formation in vibrating granular layers.*
- 2008: Workshop for participants of the Interdisciplinary Camp of of the Polish Children's Fund in Otwock *Breath spectroscopy.*
- 2006: Workshop for participants of the Polish Children's Fund *How the color of light emission depends on the dimension of a semiconductor nanostructure.*
- 2005: Workshop for participants of the Polish Children's Fund *How the color of light emission depends on the dimension of a semiconductor nanostructure.*
- 1996: Workshop for participants of the Polish Children's Fund *Interference and diffraction.*

6.3 Organizational activities

- 2012 — 2015: Member of the Scientific Council of the Institute of Physics, Polish Academy of Sciences.
- 2011 — 2015: Chairman of the Tutorial Session and member of the Program Committee of the International School and Conference on the Physics of Semiconductors, Jaszowiec.

6.4 Development of the workplace

- 2008: Creation of the microspectroscopy laboratory allowing optical investigations of single nanostructures such as quantum dots or nanowires. The setup allows to perform optical measurements such as photoluminescence or reflectivity with a diffraction limited spatial resolution, i.e., about 1 μm . There are laser sources emitting at the wavelengths of 405 nm, 473 nm and 532 nm, and a white light source. The sample is illuminated via a microscope objective through which the signal is then collected. The signal is then detected by a CCD camera coupled to a monochromator. The sample surface can be imaged on another CCD camera, which, in particular, allows to choose the proper spot for experiments. The sample is place in a cryostat, which allows to perform the measurements in the temperature range between 10 and 300 K. It also allows to connect electrical leads for measurements in electric fields. Setting up this laboratory allowed to perform the experiments, which were then published in H4, H5, H6, and H8 (entire data for H4 and H8 was collected here), and also Q1-Q4, P2, D1-D5, and Z5-Z8. Moreover, the lab is used for teaching *New materials:*

technology and design for II/III year students of Nanostructure Engineering Faculty of Chemistry/Faculty of Physics, University of Warsaw.

- 2013: Creating a setup for photon correlation and time-resolved photoluminescence measurements. The setup extends the potential of the microspectroscopy lab. Consists of a 70 ps pulsed laser emitting at 375 nm, a set of avalanche photodiodes, and two monochromators with CCD cameras. The setup allows to measure photoluminescence dynamics with 250 ps resolution and for photon correlation measurements in a Hanbur-Brown and Twiss scheme.

L. Kępczyński