Chapter 5

Luminescence of nanocrystalline ZnSe:Mn$^{2+}$

The synthesis and luminescent properties of nanocrystalline ZnSe:Mn$^{2+}$ prepared via an inorganic chemical synthesis method are described. The photoluminescence spectra show distinct ZnSe and Mn$^{2+}$ related emissions, both of which are excited via the ZnSe host lattice. The Mn$^{2+}$ emission wavelength and the associated luminescence decay time depend on the concentration of Mn$^{2+}$ incorporated into the ZnSe lattice, which is an indication of the (preferential) formation of Mn$^{2+}$ pair-states. Temperature-dependent photoluminescence spectra and photoluminescence lifetime measurements are also presented and the results are compared to those of Mn$^{2+}$ in bulk ZnSe. From the data it is concluded that the temperature dependence of the Mn$^{2+}$ emission can be explained by electron-phonon coupling to an optical phonon of the ZnSe host lattice.
5.1 Introduction

Quantum-size effects in nanocrystalline semiconductors such as CdS, CdSe, ZnS and ZnO have been studied extensively [1–6]. In some cases the method for the synthesis of nanometer sized semiconductor particles is a simple room temperature reaction in water or alcohol (e.g. CdS, ZnS or ZnO) [4–6]. This was also the case for the nanocrystals described in the first part of this thesis (chapters 2, 3 and 4). In other cases, more elaborate and challenging high temperature reactions with air and moisture-sensitive reactants are required to obtain highly efficient luminescing nanocrystals (such as CdSe) [1, 2]. In addition to undoped semiconductor nanocrystals, the luminescence of nanocrystalline semiconductors in which optically active ions are incorporated has received considerable attention, also in relation to possible applications [7, 8]. A simple wet chemical synthesis is attractive for device applications since large amounts of well-defined nanocrystals can easily be obtained in this way. As a result, many studies have focussed on ZnS and CdS doped with Mn$^{2+}$ or trivalent lanthanides [5].

Efficiently luminescing ZnS:Mn$^{2+}$ nanocrystals (with a quantum efficiency of more than 10 %) can easily be synthesized and are considered for application in low-voltage electroluminescent devices [7, 9], as was also discussed in some detail in chapter 4. However, the position of the ZnS valence band-edge is located too far from the vacuum-level to allow direct injection of holes from presently available $p$-type conducting polymers into the ZnS valence band. Better results are expected for ZnSe, which has a valence band-edge at higher energy with respect to that of ZnS [10], as will be shown in chapter 7.

Up to now, there have been no reports on the synthesis and luminescence properties of nanocrystalline ZnSe doped with a luminescent ion, such as manganese. This is probably due to the fact that the synthesis of nanocrystalline ZnSe particles is not as simple as that of ZnS particles. Undoped ZnSe particles with quantum efficiencies of 1–5 % have been obtained by a high temperature (300 °C) synthesis in the organic soap hexadecylamine [11]. It seems reasonable that such a synthesis can also be extended to include a luminescent dopant such as Mn$^{2+}$ in the ZnSe lattice.

In this chapter the preparation of nanocrystalline ZnSe particles doped with Mn$^{2+}$ is discussed. It will be shown that Mn$^{2+}$ can be incorporated into nanocrystalline ZnSe and made to luminesce by exciting in the ZnSe host lattice. To this end, photoluminescence emission and excitation spectra are presented and discussed. Furthermore, temperature-dependent luminescence and luminescence lifetime measurements are also reported and compared to results obtained for the
5.2 Experimental

The synthesis route that was used to prepare the ZnSe:Mn$^{2+}$ nanocrystals is a variation of the TOP/TOPO synthesis used for the preparation of nanocrystalline CdSe [12]. This synthesis route yields ZnSe nanocrystals with quantum efficiencies of 1−5 % [11]. Both the preparation for, as well as the actual synthesis were performed in the protective dry-nitrogen atmosphere of a glovebox. In this glovebox, the water and oxygen concentrations were both below 10 ppm.

Hexadecylamine (HDA) was used as the solvent instead of tri-$n$-octylphosphine oxide (TOPO) because its bond to zinc is weaker and it is less alkaline than TOPO [11]. If the HDA is replaced with TOPO, then the reaction does not take place. Before the synthesis was started, a 45 ml sample of HDA was heated to 310 °C in a flask. A variable amount of the manganese precursor, manganese cyclohexanebutterate powder, was dissolved in 12 ml of tri-$n$-octylphosphine (TOP) in order to obtain samples with different Mn$^{2+}$ concentrations. To this mixture 3 ml of a 1 M solution of TOPSe (previously prepared by dissolving elemental Se-powder in TOP) was added. After stirring, 0.32 g of diethylzinc was added. This solution was shaken and then added to the hot HDA using a syringe. The nanocrystals were grown at 275 °C for 4 hours. The influence of the synthesis time on the photoluminescence characteristics and the particle size is reported in chapter 6 for a comparable system. The mixture was then allowed to cool to 70 °C and the nanocrystals were precipitated by addition of 25 ml of anhydrous 1-butanol followed by 30 ml of anhydrous methanol. The residue was taken out of the glovebox, centrifuged and decanted. The samples were returned to the glovebox and washed with anhydrous methanol. Finally the samples were dried in a vacuum desiccator, and a fine white powder was obtained. This powder consists of the ZnSe:Mn$^{2+}$ nanocrystals with a HDA capping.

The chemical composition of the samples was determined using a Perkin-Elmer Optima-3000 inductively coupled plasma spectrometer. To determine the average particle diameter, X-ray powder diffractograms were measured with a Philips PW 1729 X-ray diffractometer using Cu K$_\alpha$ radiation ($\lambda = 1.542$ Å). The photoluminescence emission and excitation spectra were recorded with a SPEX Fluorolog spectrofluorometer, model F2002, equipped with two monochromators (double-grating, 0.22 m, SPEX 1680) and a 450 W xenon lamp as the excitation source. All spectra were corrected for the spectral response of the emission mo-
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...nochromator and the photomultiplier tube. The excitation spectra were also corrected for the spectral distribution of the excitation source (xenon lamp) and the excitation monochromator. Photoluminescence lifetimes were measured using the third harmonic (355 nm) of a Quanta-ray DCR YAG:Nd laser as the excitation source. The emission light was transported through a fibre optics cable to the monochromator (Acton SP-300i, 0.3 m, 150 lines/mm grating, blazed at 500 nm). The time traces were recorded using a thermoelectrically cooled photomultiplier tube in combination with a Tektronix 2430 oscilloscope. Temperature-dependent photoluminescence emission and lifetime spectra were recorded using a liquid-helium flow-cryostat equipped with a sample heater to stabilize the temperature at temperatures between 4 K and room temperature.

5.3 Results and discussion

The amounts of Mn, Zn and Se present in the ZnSe:Mn$^{2+}$ samples were measured using inductively coupled plasma analysis. Typically, about 10% of the initial Mn$^{2+}$ that was present during the synthesis was incorporated into the ZnSe lattice. The highest Mn$^{2+}$ concentration in the ZnSe nanocrystals was found to be 3%. When the Mn$^{2+}$ precursor concentration was high enough for the incorporated Mn$^{2+}$ concentration to be greater than 1%, the yield became very low. This low yield may be due to the organic residue from the Mn$^{2+}$ precursor which can hinder the formation of the ZnSe nanocrystals. Because of this low yield, only the samples that had a Mn$^{2+}$ concentration less than 1% were used in the measurements that are discussed below.

5.3.1 X-ray diffractograms

Figure 5.1 shows the X-ray diffraction pattern for a ZnSe:Mn$^{2+}$ sample containing 0.4% of Mn$^{2+}$. This pattern is much more complicated than that measured for nanocrystalline ZnS:Mn$^{2+}$, such as the pattern shown in figure 2.1. The two sharp peaks located at 38° and 44.5° are caused by the aluminum sample holder and can be ignored. However, at least eight more (small) sharp peaks can be identified in figure 5.1, as well as three broad bands. These sharp peaks cannot be related to the ZnSe nanocrystals. They may result from crystalline hexadecylamine in the capping layer surrounding the nanocrystals, or to residue from the chemical synthesis used to prepare the nanocrystals.

The three broad bands shown in figure 5.1 are likely to be due to the ZnSe
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Figure 5.1: X-ray diffractogram of a ZnSe:Mn$^{2+}$ sample containing 0.4 % of Mn$^{2+}$. Similar patterns were obtained for other Mn$^{2+}$ concentrations. The dashed line through the data is a Gaussian fit of the broad band centered at $2\theta = 53.5^\circ$.

nanoparticles. These values were also expected, as according to the literature, the most intense lines correspond to $d$-values of 3.26, 2.00, and 1.71 [13]. As a result, the expected peak maxima are located at $2\theta = 27.4^\circ$, $2\theta = 45.4^\circ$ and $2\theta = 53.6^\circ$, according to equation (2.5). A Gaussian fit of three broad bands shown in figure 5.1 results in peaks at $2\theta = 27.5^\circ$, $2\theta = 45^\circ$ and $2\theta = 53.5^\circ$, which is in good agreement with the expected values.

Due to the many other peaks in the pattern shown in figure 5.1, an accurate fit of the principal X-ray diffraction band, at $2\theta = 27.5^\circ$, is not possible. Fortunately, a fit of any one of the broad bands will suffice to calculate the diameter of the nanocrystals by means of the Debye-Scherrer equation, as shown in equation (2.3). Therefore, the peak at $2\theta = 53.5^\circ$ could be used for the fitting. As can be seen from the dashed line through the data in the interval from $2\varphi = 51^\circ$ to $2\varphi = 56^\circ$, an accurate fit of this peak is possible. From this fit, and others like it for the different Mn$^{2+}$ concentrations, it was calculated that the nanocrystals have a diameter $d$ in the range 3–4 nm. No relation between the size of the nanocrystals and the Mn$^{2+}$
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Figure 5.2: Photoluminescence emission spectra for nanocrystalline ZnSe:Mn\(^{2+}\) samples with different Mn\(^{2+}\) concentrations, as indicated in the figure. All spectra were measured at room temperature and the excitation wavelength was 330 nm. The symbols (squares, circles, crosses, triangles and diamonds) are used to label the different spectra and the drawn lines are the measured curves. This is the case for all figures in this chapter. Relative intensities can be compared.

concentration could be observed.

5.3.2 Photoluminescence excitation and emission

Figure 5.2 shows the photoluminescence emission spectra of several nanocrystalline ZnSe:Mn\(^{2+}\) samples with an incorporated Mn\(^{2+}\) concentration between 0 % and 0.9 %. The measurement conditions were identical in all cases and therefore relative intensities can be compared. The photoluminescence band centered at around 430 nm is attributed to the excitonic luminescence of the ZnSe host lattice. The band centered at \(\sim 570\) nm is attributed to the \(^{4}T_1 \rightarrow ^{6}A_1\) transition in the Mn\(^{2+}\) ion. The position of the Mn\(^{2+}\) emission is similar to that for Mn\(^{2+}\) in bulk ZnSe [14, 15]. On the lower energy side (600–640 nm) a third emission band is usually found for bulk ZnSe:Mn\(^{2+}\). This band is assigned to a self-activated lumini-
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nescence, probably due to $\text{Cl}_{\text{Se}}^{\bullet} - \text{V}_{\text{Zn}}^{{\circ}}$ donor-acceptor pairs. (Here the Kröger-Vink notation is used for identifying defect states [16]). The observation that this self activated luminescence is absent (or very weak) indicates that the concentration of $\text{Cl}_{\text{Se}}^{\bullet} - \text{V}_{\text{Zn}}^{{\circ}}$ pairs in the ZnSe nanocrystals is low. This is likely to be due to either the small size of the nanocrystals (low probability for the presence of both types of defect in one nanocrystal); or to the purity of the chemicals used for the synthesis; or an effect of the confinement of the electron-hole pair: because of this there is no energy migration possible to the $\text{Cl}_{\text{Se}}^{\bullet} - \text{V}_{\text{Zn}}^{{\circ}}$ donor-acceptor pair.

The quantum efficiency of the various samples was calculated by comparing the integrated intensity of the emission spectrum with that of the commercial lamp phosphor $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ (BAM), which was kindly provided by Philips. This phosphor has a known quantum efficiency of about 90 % when excited at 300 nm [17]. The emission spectra of BAM and of the ZnSe:Mn$^{2+}$ sample were recorded under identical conditions. If the ratio of the integrals of the emission spectrum of the sample and that of BAM is denoted by $x$, the the quantum efficiency of the sample is simply $x \cdot 90 \%$, when one assumes that the absorbance of the sample and that of BAM are identical.

The total luminescence quantum efficiency (indicated in figure 5.2) shows a large decrease when a small concentration of Mn$^{2+}$ is incorporated into the ZnSe host lattice. This is a bit surprising, because it is known from the literature that efficient energy transfer from the ZnSe host lattice to the Mn$^{2+}$ dopant is possible [18]. Apparently the decrease of the ZnSe related emission is not only due to energy transfer to Mn$^{2+}$, which does not affect the quantum efficiency. The drop in the quantum efficiency from 2.5 % to 0.4 % for the incorporation of 0.2 % Mn$^{2+}$ therefore indicates that nonradiative quenching centers are also formed as a by-product of the synthesis including the Mn$^{2+}$ precursor. This is probably due to the organic residue from the Mn$^{2+}$ precursor, which may induce defects in the nanocrystal, or result in efficient quenching states on its surface.

At higher Mn$^{2+}$ concentrations, the energy transfer to Mn$^{2+}$ becomes more efficient and the intensity of the yellow Mn$^{2+}$ emission increases. For 0.9 % Mn$^{2+}$ the quantum efficiency has increased to 2.7 %, just above that of the ZnSe related emission in the undoped sample. The present results are typical for one concentration series of Mn$^{2+}$ doped ZnSe nanocrystals. Since the quantum efficiencies of doped and undoped nanocrystalline semiconductors are strongly dependent on small variations in the synthesis procedure, higher quantum efficiencies can be expected on optimizing the synthesis procedure. Better results may also be obtained with another type of Mn$^{2+}$ precursor.
Figure 5.3: Photoluminescence excitation spectra for the ZnSe: 0.2% Mn$^{2+}$ sample. The spectra were measured at room temperature and the emission wavelengths are indicated in the figure. The values of $\phi$ for the two curves cannot be compared.

The observed photoluminescence emission energies for the Mn$^{2+}$ related luminescence, obtained from a Gaussian fit of the Mn$^{2+}$ related photoluminescence peak using the relative emitted photon flux per constant energy interval as a function of the energy, are indicated in figure 5.2. Due to the high quality Gaussian fits, the accuracy in the obtained emission energies was better than 1 meV. A shift in the maximum of the Mn$^{2+}$ emission to lower energy is observed for increasing Mn$^{2+}$ concentrations. This shift is possibly due to the formation of pairs of Mn$^{2+}$ ions at higher concentrations. It is well known that the emission of Mn$^{2+}$ pairs can be at lower energy than that of single ions [19]. Lifetime measurements presented below provide additional evidence for the formation of exchange-coupled Mn$^{2+}$ pairs at higher Mn$^{2+}$ concentrations.

Figure 5.3 shows the photoluminescence excitation spectra of both the ZnSe and the Mn$^{2+}$ related emissions. In this figure, $\phi$ denotes the photon flux per constant wavelength interval. Both spectra show a clear maximum for excitation at $\sim$370 nm. The steep increase beyond 390 nm in the excitation spectrum for the
ZnSe related emission is due to the detection of scattered excitation light which is not rejected by the monochromator, since the wavelength of the emission monochromator ($\lambda = 418$ nm) is close to the excitation wavelength. The position of the excitation maximum was found to vary slightly from sample to sample; a small variation in particle size (and thus in the bandgap) can explain such differences. This agrees with the results from X-ray diffraction measurements. Using the known values of the material parameters in ZnSe ($m_e^* = 0.17m_0$ [20], $m_h^* = 0.60m_0$ [21], $\epsilon_r = 8.1$ [22] and $E_g = 2.8$ eV [22]), the Brus equation (1.7) that relates the energy of the bandgap in electron volts to the radius of the nanocrystals in nanometers [3] becomes

$$E_g(r) = 2.8 - \frac{0.32}{r} + \frac{2.84}{r^2}. \quad (5.1)$$

From equation (5.1) it is clear that the excitation maximum of 370 nm (3.35 eV), as found from figure 5.3, corresponds to a crystal radius of $r \approx 2$ nm, which is in good agreement with the value of $d \approx 3$–4 nm as was determined by X-ray powder diffraction.

The fact that both the ZnSe and the Mn$^{2+}$ emissions have the same excitation maximum indicates that the excitation of the divalent manganese takes place through excitation of the ZnSe host lattice, followed by energy transfer to the Mn$^{2+}$ ion. This agrees with the qualitative observation based on figure 5.2 that incorporation of Mn$^{2+}$ in the ZnSe lattice results in a decrease of the ZnSe related photoluminescence and a concomitant increase in the Mn$^{2+}$ photoluminescence. Efficient energy transfer to Mn$^{2+}$ centers incorporated in ZnSe has been well studied in bulk ZnSe:Mn$^{2+}$ [23] and efficient transfer was expected to occur in nanocrystalline ZnSe:Mn$^{2+}$, as is indeed observed (although not with the same efficiency as can be seen from figure 5.2).

Figure 5.4 shows the excitation spectrum of the Mn$^{2+}$ related photoluminescence at higher energy. The spectral range probed in this experiment, the UV to VUV range, is difficult to access because very few tunable radiation sources with a high photon flux are available for this range. Therefore, these measurements were performed at the HIGITI experimental station [24] of the Synchrontronstrahlungsabor HASYLAB at the Deutsche Elektronen-Synchrotron DESY in Hamburg (Germany). In the excitation spectra the ultimate spectral resolution is better than 0.5 nm [25] and all spectra were corrected for the spectral intensity distribution of the synchrotron radiation (using a spectrum provided by DESY). The relatively poor resolution in this spectrum is due to the short time that was available to perform this measurement.
Figure 5.4: Excitation spectrum of the Mn\(^{2+}\) related emission (measured at 580 nm) for high energy photons. The spectrum was measured using the HIGITI station (DESY, Hamburg, Germany) and recorded at 10 K.

Figure 5.4 shows three additional excitation bands for the Mn\(^{2+}\) related emission, at the wavelengths ~200 nm, ~155 nm and ~130 nm. The three excitation bands shown in figure 5.4, as well as the one observed in figure 5.3, can all be related to the ZnSe host lattice. This would imply that there are four excitation bands of the ZnSe below 10 eV: 3.35 eV (370 nm), 6.2 eV (200 nm), 8 eV (155 nm) and 9.5 eV (130 nm). It is interesting to note that the energy separation between these subsequent excitation bands decreases: 3.35 eV, 2.85 eV, 1.8 eV and 1.5 eV. This would also be expected as these values are a measure for the Fourier-components of the periodic potential (which must decrease to ensure convergence of the total Fourier sum). The third excitation band of the ZnSe, at roughly 8 eV, agrees rather well with a known excitation maximum of bulk ZnSe which involves a transition at the \(\Gamma\) point in \(k\)-space. However, a detailed assignment of each of these transitions was not performed because the band structure for a nanocrystal is likely to be different from that of a bulk crystal. Unfortunately, detailed band structure calculations for a ZnSe nanocrystal are not available. Note that in this discussion it
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is assumed that the hexadecylamine layer surrounding the nanocrystals is transparent over this energy range. Another explanation of the structure seen in figure 5.4 could therefore be that these ‘excitation bands’ are in fact due to the absorption bands of hexadecylamine.

5.3.3 Luminescence lifetime

The time dependence of the ZnSe and Mn$^{2+}$ related luminescence intensity after pulsed excitation was measured for the samples shown in figure 5.2. Figure 5.5 shows the Mn$^{2+}$ luminescence decay curves (measured at 570 nm) for all the samples, measured at room temperature and scaled at $t = 0$. Note that because the spectra were scaled at $t = 0$, the baselines (i.e. the background intensities) are not the same due to the differences in quantum efficiency from sample to sample. Single-exponential fits of the decay curves up to 1 ms are shown as lines through the data. In all cases a good single-exponential fit was possible using a lifetime of the order of 200 µs. The exact values of the lifetimes are indicated in the figure. Even though
the fits shown in figure 5.5 describe the experimental data rather well, the decay is not purely single exponential. Therefore, the lifetime depends slightly on the time interval used in the fitting procedure. The samples containing a higher Mn$^{2+}$ concentration have shorter lifetimes and a drop from $\sim$290 $\mu$s to $\sim$190 $\mu$s is observed between 0.2 $\%$ Mn$^{2+}$ and 0.9 $\%$ Mn$^{2+}$. Finally, a fast ($\sim$100 ns) component of the lifetime is also found. This component is assigned to the ZnSe emission, rather than the Mn$^{2+}$ emission. This is expected to be correct, because the ZnSe related emission overlaps slightly with the Mn$^{2+}$ luminescence spectrum. A similar effect has been observed for nanocrystalline ZnS:Mn$^{2+}$ [26, 27].

The interpretation of the measured lifetimes and the concentration dependence is not straightforward. In spite of extensive research on bulk ZnSe:Mn$^{2+}$, the radiative lifetime of the Mn$^{2+}$ emission (from single ions) is not well established; values between 30 and 800 $\mu$s have been reported [14, 15, 28]. At room temperature the lifetime is reduced by thermal quenching, which has been found to be sample dependent. The concentration also influences the lifetime; even at Mn$^{2+}$ concentrations as low as 1 $\%$ a reduction in the lifetime has been reported [15]. Due to the uncertainty in the single ion radiative lifetime and the non-exponential character of the luminescence decay curve, it is difficult to derive quantitative information from the luminescence decay results of figure 5.5. However, two qualitative conclusions can be made.

Firstly, the lifetime of the Mn$^{2+}$ emission in ZnSe is of the order of hundreds of microseconds, which is much shorter than the lifetime of the Mn$^{2+}$ emission in ZnS (where a lifetime of 1.8 ms was found). This has also been observed for the bulk materials and is explained by stronger spin-orbit coupling due to the heavier Se$^{2-}$ ligands in comparison to S$^{2-}$ [28].

Secondly, the lifetime of the emission is shorter at higher Mn$^{2+}$ concentrations ($\sim$290 $\mu$s at 0.2 $\%$ Mn$^{2+}$, as compared to $\sim$190 $\mu$s at 0.9 $\%$ Mn$^{2+}$). It is known that due to exchange interaction the spin selection rule is partially lifted and the $^{4}T_1 \rightarrow ^{6}A_1$ transition in the Mn$^{2+}$ becomes more allowed at higher Mn$^{2+}$ concentrations [19]. This results in the fact that the lifetime of the Mn$^{2+}$ emission will be reduced at higher Mn$^{2+}$ concentrations when exchange-coupled Mn$^{2+}$ pairs are formed.

It seems reasonable to attribute the shortening of the lifetime (shown in figure 5.5) and the shift in the luminescence emission energy (shown in figure 5.2) to the presence of Mn$^{2+}$ pair-states. However, the concentration range in which this effect is observed is too low to be explained by random pair formation: for Mn$^{2+}$ concentrations in the range of 0.2 $\%$ – 0.9 $\%$, it is calculated that the percentage
of Mn$^{2+}$ pair-states will be between 1.9 % and 8.7 % based on random pair formation [29]. This implies that (assuming random pair formation) roughly 90 % of the luminescence signal should be generated by isolated Mn$^{2+}$ ions. The shift in the luminescence emission energy (shown in figure 5.2) as well as the shortening of the lifetime (shown in figure 5.5) both seem too large to be explained by less than 10 % of the total Mn$^{2+}$ concentration. Therefore, this suggests that preferential pair-formation is responsible for the relatively large effect of the Mn$^{2+}$ concentration on the emission energy and the luminescence lifetime.

Another explanation for the shortening of the Mn$^{2+}$ luminescence lifetime and the shift in the luminescence emission energy, not requiring preferential pair formation, could be the more efficient trapping of electron-hole pairs after bandgap excitation by the Mn$^{2+}$ pair-states compared to single ions. As a result of this efficient trapping, the (low concentration of) Mn$^{2+}$ pair-states could be responsible for the majority of the luminescence. This has been suggested previously for bulk ZnSe:Mn$^{2+}$ [30].

The ZnSe luminescence decay curves (measured at 420 nm) were found to have ~100 ns components as well as components that were too fast to be measured with the experimental setup used to determine the Mn$^{2+}$ lifetime. The lifetime of the ZnSe related luminescence has therefore been measured using the much faster setup available at the HIGITI station at the DESY synchrotron in Hamburg. Figure 5.6 shows a decay spectrum of the ZnSe related emission (measured at 420 nm) recorded at 10 K under 370 nm excitation. The ZnSe luminescence has a single-exponential decay, as can be seen from the line through the data. The lifetime was found to be 3.6 ns at 10 K, which is reasonable for this (spin-allowed) transition. No measurements of the lifetime of the luminescence of bulk ZnSe have been published, and therefore no comparison can be made. However, it is expected that the lifetime for bulk ZnSe will be comparable to that found for the nanocrystalline material.

### 5.3.4 Temperature dependence

Figure 5.7 shows temperature-dependent measurements of the photoluminescence spectra for a ZnSe: 0.7 % Mn$^{2+}$ sample under 330 nm excitation. It is clear that there is a strong quenching of the ZnSe and Mn$^{2+}$ related photoluminescence intensities. This has also been reported for bulk ZnSe:Mn$^{2+}$ [28, 31]. A detailed discussion of the quenching behavior, as well as an explanation of the mechanism (due to Auger quenching) have been reported in Ref. [32].

A clear shift of the ZnSe related photoluminescence emission energy to longer
Figure 5.6: Time dependence of the ZnSe related emission intensity. The thick line is a single exponential fit of the data resulting in the 3.6 ns lifetime indicated in the graph. The emission wavelength was 420 nm and the excitation wavelength was 370 nm. The measurement was performed at 10 K using the HIGITI setup at DESY (Hamburg). The pulse duration was 150 ps and the pulse separation was 192 ns. The final resolution that can be obtained is about 200 ps, mainly due to the response-time of the photomultiplier.

Wavelengths is also observed for increasing temperature in figure 5.7. The data is shown in figure 5.8(a), where the emission energy was obtained from a Gaussian fit of the emitted photon flux per constant energy interval as a function of energy. Note that for low temperatures (roughly below 50 K) a shift of the ZnSe related emission energy to higher energy is observed. This effect was also reported in chapter 3 for the luminescence of nanocrystalline ZnS:Mn$^{2+}$ and is related to the detrapping of charge carriers from shallow defect states at elevated temperature. The shift of the ZnSe related emission energy (for temperatures higher than 50 K) could be fitted very well using the standard Varshni equation for the temperature dependence of the bandgap of a semiconductor [33]

$$E_g(T) = E_0 - \frac{\alpha T^2}{T + \beta},$$

(5.2)
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Figure 5.7: Temperature-dependent photoluminescence spectra for the ZnSe:0.7% Mn$^{2+}$ sample. Note the logarithmic intensity axis. The excitation wavelength was 330 nm and the intensities can be compared.

where $E_0$ represents the bandgap at 0 K and $\alpha$ and $\beta$ are fitting parameters. It is known from the literature that $\beta$ is of the order of the Debye temperature of the semiconductor. This equation takes into account both the change in lattice parameter and the temperature dependence of the electron-lattice interaction. As mentioned earlier (in chapter 3), equation (5.2) was originally derived in the infinite crystal approximation and is used to analyze bulk semiconductor systems. It is not immediately obvious that this equation also applies to nanocrystalline semiconductors which have a different band-structure and a different phonon density of states.

The temperature dependence of the ZnSe related photoluminescence could be fitted with equation (5.2), as is shown by the line through the data in figure 5.8(a). From these fits values of $\alpha = (9 \pm 3) \cdot 10^{-4}$ eV/K and $\beta = (3.8 \pm 1) \cdot 10^2$ K were found. These values compare well with those found for bulk ZnSe ($\alpha = 7.5 \cdot 10^{-4}$ eV/K and $\beta = 295$ K [34]).

Figure 5.8(b) shows the change in the Mn$^{2+}$ related photoluminescence emis-
Figure 5.8: Temperature dependence of the emission energy for a ZnSe: 0.7% Mn\(^{2+}\) sample. (a) Maximum energy of the ZnSe related emission energy. The line through the data is a fit of equation (5.2). (b) Temperature dependence of the Mn\(^{2+}\) related emission energy. The line through the data is a fit of equation (5.3) with a phonon energy of $\hbar \omega = (27 \pm 2) \text{meV}$.

The emission energy as a function of the temperature. Again, the emission energy was obtained from a Gaussian fit as discussed before. The shift of the Mn\(^{2+}\) emission energy to shorter wavelength for increasing temperature has also been observed for bulk ZnSe:Mn\(^{2+}\) [35]. The measured blue-shift can be fitted very well using the temperature dependence of the emission energy of the optical transition resulting from electron-phonon interaction as obtained by McCumber and Sturge, [36]

$$E(T) = E_0 + C T^4 \int_0^{\hbar \omega} \frac{d \epsilon}{e^\epsilon - 1} .$$  \hspace{1cm} (5.3)

This is shown by the line through the data in figure 5.8(b). In equation (5.3) $E_0$ is the emission energy at 0 K, $\hbar \omega$ represents the energy of the lattice vibration that couples to the optical transition through the electron-phonon interaction and $C$ is a (positive) fitting constant. The reason that this equation (strictly speaking
only valid for the weak-coupling case) can be used in this case (involving strong coupling), has been discussed in detail in chapter 3. Figure 5.8(b) shows that a good fit of the data can be obtained using a phonon energy of $\hbar \omega = (27 \pm 2)$ meV in equation (5.3).

The data shown in figure 5.7 has also been used to determine the half-width at half maximum (HWHM) of the Mn$^{2+}$ related emission band as a function of the sample temperature. This bandwidth was also determined from a Gaussian fit to the emission profile using the relative photon flux per constant energy interval as a function of energy. Due to the electron-phonon coupling this bandwidth changes with temperature, as can be seen from the data shown in figure 5.9. The emission bandwidth is an increasing function of the sample temperature and can in the strong coupling limit be written as [37]

$$
\Gamma(T) = \Gamma_0 \sqrt{\coth \left( \frac{\hbar \omega}{2k_B T} \right)}.
$$  \hspace{1cm} (5.4)
Here $\Gamma_0$ represents the bandwidth at zero temperature and $\hbar\omega$ is the energy of the lattice vibration that couples to the optical transition. The origin of this equation has also been discussed in detail in chapter 3. The fact that the data in figure 5.8(b) and the data in figure 5.9 could both be fitted using the same value for the phonon energy, $\hbar\omega = (27 \pm 2)$ meV, supports the validity of equations (5.3) and (5.4) in this case. This phonon energy agrees with the energy of a known optical phonon in bulk ZnSe [38]. Note that also here the thermal expansion of the lattice can explain the shift of the Mn$^{2+}$ related emission, similar to what was discussed in chapter 3.

The temperature dependence of the ZnSe related bandwidth could not be obtained with an acceptable accuracy. This is due to the fact that the intensity of the ZnSe related emission is much lower than that of the Mn$^{2+}$ related emission (remember that the intensity axis in figure 5.7 is logarithmic). As a result, a slightly different fitting interval gave equally good fits of this emission (similar $\chi^2$ values), but with large differences in the bandwidth. This implies that the error was too large to allow for meaningful conclusions to be drawn from this data. Therefore this data is not presented here.

Finally, also the temperature dependence of the Mn$^{2+}$ related photoluminescence lifetime was determined; figure 5.10 shows results for a ZnSe:0.4 % Mn$^{2+}$ sample. In contrast to previous results for ZnS:Mn$^{2+}$, a temperature-induced decrease of the lifetime is observed. When this temperature-induced decrease of the Mn$^{2+}$ lifetime is fitted on the basis of a simple thermally-activated non-radiative decay path competing with radiative recombination,

$$\frac{1}{\tau(T)} = \frac{1}{\tau_0} + \frac{1}{\tau_{NR}} \exp \left[ \frac{-\Delta E}{k_B T} \right],$$

(5.5)

a good fit of the data can be obtained, as can be seen from the line through the data in figure 5.10.

The fit using equation (5.5) yields values for $\tau_0 = 303$ $\mu$s, $\tau_{NR} = 200$ $\mu$s and $\Delta E = (26 \pm 2)$ meV. The value of $\Delta E$ is found to be independent of the Mn$^{2+}$ concentration present in the ZnSe lattice. The decrease in lifetime can be explained by thermally-activated energy transfer to quenching centers since, in the same temperature regime in which the luminescence lifetime becomes shorter, the luminescence intensity decreases.
5.4 Conclusions

This chapter presents a chemical synthesis method for powders of ZnSe nanocrystals (average particle diameter in the range of 3–4 nm) doped with Mn$^{2+}$. The photoluminescence emission spectra of these samples show a ZnSe related near band edge emission at ~440 nm and a Mn$^{2+}$ related band at ~570 nm. The wavelength of the Mn$^{2+}$ related emission shifts to lower energy for increasing amounts of Mn$^{2+}$ incorporated into the ZnSe lattice. The photoluminescence excitation spectrum shows that the divalent manganese can be excited through the ZnSe host lattice. High-energy excitation spectra reveal that the ZnSe host lattice has four excitation bands below 10 eV. The Mn$^{2+}$ luminescence decay curves yield a lifetime of ~290 μs at room temperature, which decreases with increasing [Mn$^{2+}$]. The decrease in lifetime and emission energy of the Mn$^{2+}$ related emission for increasing Mn$^{2+}$ concentration may be due to the (preferential) formation of Mn$^{2+}$ pairs in the nanocrystal. The temperature dependence of the Mn$^{2+}$ lifetime can

![Figure 5.10: Temperature-dependent lifetimes of the Mn$^{2+}$ photoluminescence for a ZnSe:0.4% Mn$^{2+}$ sample. Pulsed excitation at 355 nm was used. The line is a fit to the data for the thermally-activated process described by equation (5.5) using an activation energy of $\Delta E = (26 \pm 2)$ meV.](image-url)
be explained by a temperature-activated quenching with an activation energy of 26 meV. The ZnSe related luminescence wavelength has a temperature-induced shift similar to that of bulk ZnSe. The self-activated emission (expected at ~640 nm), often observed in bulk ZnSe:Mn$^{2+}$, is not present in these nanocrystals.

References

References

Luminescence of nanocrystalline ZnSe:Mn$^{2+}$