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PICOSECOND ENERGY TRANSFER BETWEEN EXCITONS AND DEFECTS IN II-IV SEMICONDUCTORS

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ABSTRACT

The luminescences of bound excitons in various II-IV semiconductors are studied by means of time resolved spectroscopy at liquid helium temperatures. A general trend of increasing lifetimes with increasing binding energies is in reasonable agreement with the theory of Rashba and Gurgenishvili indicating a predominant radiative decay. It is shown that the investigation of the dynamics of weakly bound excitons provides the possibility to determine parameters of the free exciton. An effective exciton mass of $1.06m_0$ for ZnO and a free exciton oscillator strength of 0.0014 for ZnS are determined. The limits of the model in case of deeply bound excitons as well as the nonradiative decay channels are discussed. The observed luminescence risetimes due to the formation of bound exciton complexes after generation of free excitons are investigated.

Introduction

In II-IV compounds nearby the free exciton resonances a lot of sharp lines dominate the emission spectra[1]. These lines are due to the radiative decay of excitons weakly bound to different defects always present in these compounds. Due to the high formation probability of such complexes they are the dominant decay channel for intrinsic excitations (e.g. free excitons) in these semiconductors. Even low impurity concentrations suppress the free exciton luminescence due to a drastic shortening of their lifetimes[2]. The giant oscillator strengths connected with bound excitons correspond to extremly short radiative lifetimes, which strongly reactivated the interest in recent years[3,4,5], since the bound excitons become good candidates for fast nonlinear optical devices, suggested for optical or opto-electronic data processing.

In this paper we report on time resolved spectra of free and bound excitons in ZnO, ZnS, CdS and ZnSe at low temperatures. Low excitation densities are employed, since otherwise biexcitons and other nonlinearities superimpose the dynamical behaviour of the bound excitons. The obtained data are compared to recent results for ZnO[5], ZnSe[3,6] and CdS[7] and discussed in the framework of the theory developed by Rashba and Gurgenishvili[8,9] in order to determine the parameters controlling the relevant decay mechanisms. Thereby, it is demonstrated that the investigation of the decay dynamics of weakly bound excitons gives a valuable feedback about basic parameters of free excitons, e.g. their oscillator strength or effective mass. The results are compared to those of excitons deeply bound to Ni-centres and to calometric absorption results.

Experimental

The experimental arrangement consists of an actively modelocked Nd-YAG laser which is either frequency-tripled to pump synchronously a dye laser operating with stilbene 3 for band-band excitation of ZnSe and CdS, or frequency-doubled to pump R6G-dye, subsequently again frequency-doubled to excite ZnS and ZnO above the bandgap. A cavity dumper is used to lower the pulse repetition rate to 3.8MHz and to increase the peak power. The system delivers pulses of about 3ps duration and an average power of up to 300mW. During the luminescence experiments average excitation densities of $0.5 mW/mm^2$ or less are used. The transient luminescence is detected through a 0.75m monochromator by means of time-correlated single photon counting using a micro-channel plate photomultiplier tube (Hamamatsu R2809U). The instrumental time resolution is about 50ps, allowing the determination of lifetimes down to 15ps by deconvolution technics. The results of the subsequent convolutions are given as full lines in fig.1-4. The origin of the luminescence transients is checked by means of time delayed luminescence spectroscopy.

In the analysis of the observed luminescence transients I(t) the formation time τ_r and the decaytime τ_d of bound exciton complexes have to be taken into acount:

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$$I(t) \sim (\tau_r - \tau_d)^{-1} [\exp(-t/\tau_r) - \exp(-t/\tau_d)]$$

The rising part of the luminescence intensity depends on the smaller one between τ_r and τ_d and the decaying part on the larger one. To determine the decaytime we performed pump-and-probe measurements under resonant excitation conditions. Average pump powers of about 20mW and probe powers of less than 0.5mW are used.

Results

The time dependence of the bound exciton complexes in high-quality ZnO rods have been investigated. The insert of fig.1 shows the time integrated luminescence spectrum of a not intentionally doped crystal recorded under the same conditions as used for the time resolved measurements. Emission lines due to different localized bound exciton complexes occur. The chemical nature of the participating defects is still not clear but lines near the resonances I_3 at 3.3662eV and I_4 at 3.3629eV have been assigned to (D^0,X)-complexes[10] and the lines I_6 (3.3606eV), I_7 (3.3600eV) and I_9 (3.3567eV) are identified as neutral acceptor bound excitons[11]. The transients of the different bound exciton emission lines, fig.1, reveal a trend of increasing lifetime with increasing binding energy. Only the I_4-complex shows a pecularity, its lifetime is longer than those of the stronger localized I_6- and I_7-complexes. The obtained decaytimes are summarized in tab.I and in qualitative agreement with results reported for I_7 and I_{10}[5]. The observed risetimes of about 60ps to 80ps in the bound exciton luminescences are correlated to the dynamics of the free A-exciton. Under the employed excitation conditions the A-exciton decays almost exponential with a time constant of (60±10)ps during the first 200ps and afterwards becomes slower, probably due to a saturation of the bound exciton recombination channels. This indicates the formation of bound exciton complexes as dominant process lowering the free exciton density in the investigated sample. It has to be noted that for the lines I_4 to I_9 at longer times an additional weak (about 1%) component with a time constant of 1.9ns is observed. Time delayed luminescence spectra show that this slow component is connected with the respective bound exciton emissions, too, indicating a unique slow bound exciton formation channel whose origin is still unclear. In weakly doped crystals the bound exciton emission lines become broader, but at least the decaytimes of the (A^0,X) complexes remains unaltered. Additionally, the free exciton lifetime as well as the luminescence risetimes decrease simultaneously.

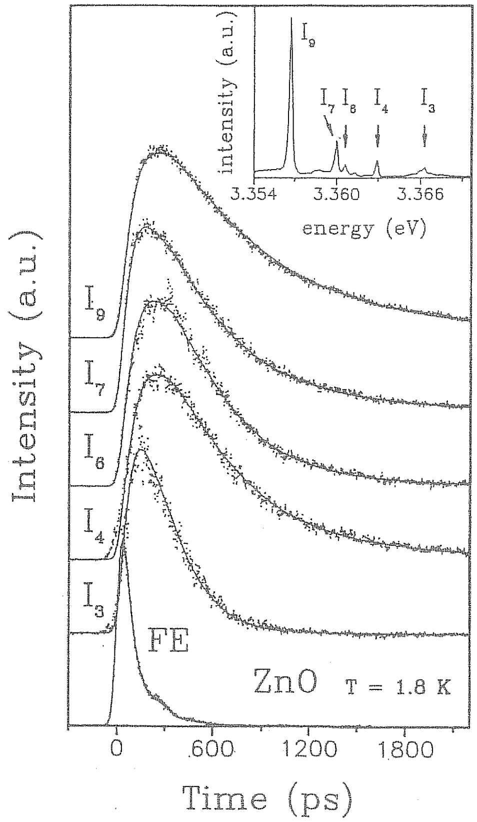

fig.1: Luminescence transients of exciton emissions in ZnO excited at 4.12eV. The insert gives the time integrated luminescence spectrum.

The transients of different exciton emission lines of a CdS crystal containing 0.1ppm Ni are shown in fig.2. Not intentionally as well as In- or Ni-doped samples show again that the free exciton decaytime and the bound exciton risetimes decrease simultaneously down to 25ps in doped crystals whereas the decay of the bound exciton complexes remains unaltered. The (A^0,X)-complex (I_1, 2.5356eV) has a lifetime of 650±20ps and the (D^0,X)-complex (I_2, 2.5467eV) has a lifetime of 100±20ps, see tab.I. This values are somewhat shorter than results reported by Henry and Nassau[7], possibly indicating concentration quenching in our crystals or too high excitation densities. We have to exclude both possibilities: the experimental results show no resolveable influence of the different used dopand's concentrations ($\leq 10^{16}cm^{-3}$) on the bound exciton lifetimes and luminescence spectra recorded under the employed experimental conditions show no biexciton luminescence, the so called M-band which occur near I_2 and is slower anyhow[12]. In order to investigate the bound exciton dynamics under resonant excitation and to exclude effects of the free exciton density we performed pump-and-probe measurements. Fig.3 shows the results obtained for the I_2-absorption of a thin CdS sample. The insert gives the absorption spectrum ($E \perp c$) with the I_2-resonance at 2.5467eV as observed with the pump beam. No influence of the excitation density is resolved but the much more sensitive pump-and-probe technics reveal small absorption changes induced by the pump-beam. The absorption of the pump-pulse leads to a saturation of the I_2-absorption, whereby the temporal increase of the saturation follows the integral of the pump-pulse. Subsequently, the saturation decays with 110±20ps corresponding well to the 100ps determined in time resolved luminescence experiments. (The decay time of the (A^0,X)-complex has been confirmed, too.) During the temporal coincidence of pump- and probe-pulses fast changes of the pump-and-probe signal are observed, see fig.3. The amplitude ratios of the induced absorption and transmission as well as of the I_2-saturation are sensitive to the experimental conditions indicating three almost independent processes. The induced absorption is connected with the pulse duration wheras the induced fast transmission is connected with the coherence time of the pulses. Therefore, we propose that the fast absorptive change is due to two-photon absorption not connected with the (D^0,X)-complex (it is also seen besides the resonance) and the fast transmittive change to be due to the coherence peak often observed in pump-and-probe signals.

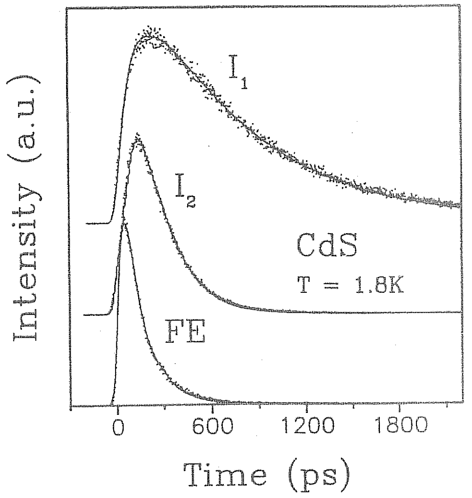

fig.2: Luminescence transients of exciton emissions in CdS excited at 2.78eV.

Recently, the I_3- and the I_5-emission line sets occuring in high quality ZnS crystals have been attributed to two different (A^0,X)-complexes[13]. The insert in fig.4 gives the time integrated luminescence spectrum of a typical sample as observed under time resolved conditions. The respective threefold finestructure of the two lines is not resolved due to the experimental resolution. The A-exciton at 3.8000eV is clearly resolved in time delayed spectra. The luminescence transients in fig.4 show exponential decays with 285ps and 150ps for the I_3- and the I_5-complexes, respectively. The free exciton decays almost exponential with (15±10)ps over one decade followed by a weak second component with 150ps corresponding to the I_5-lifetime. Obviously, the impurity correlated processes dominate the lowering of the free exciton concentration but saturate at longer times. Possibly, the reported 'hot'-lines[13] indicate a

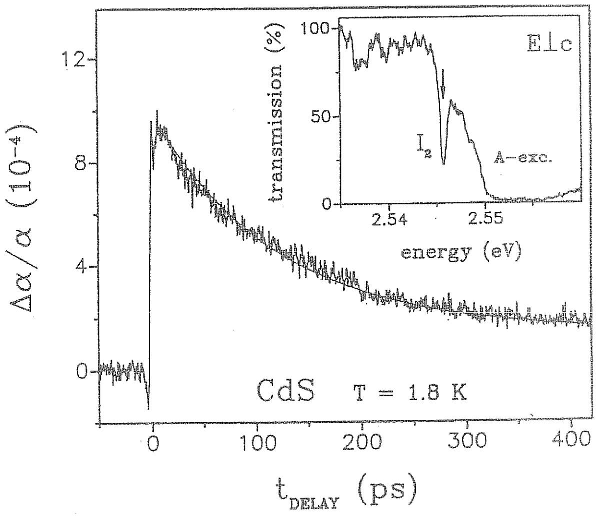

fig.3: Pump-and-probe signal of the I_2 absorption in CdS. The absorption is shown in the insert (E_{pump}, $E_{probe} \perp c$).

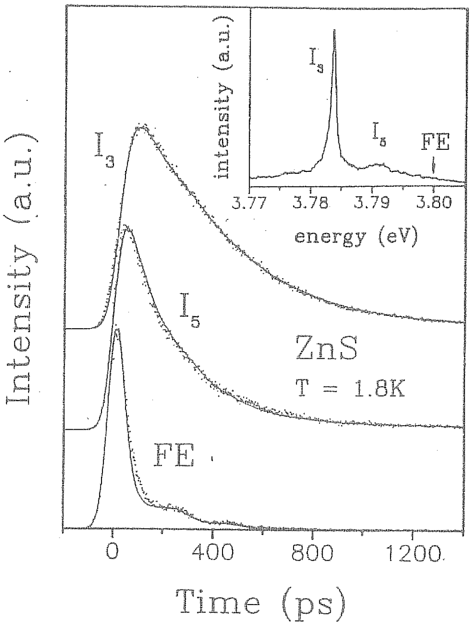

fig.4: Luminescence transients of exciton emissions in ZnS excited at 4.12eV. The insert gives the time integrated luminescence spectrum.

slow thermalization in the ground states of the (A^0,X)-complexes compared to their lifetimes.

On weakly Na- and Li-doped ZnSe samples the free exciton (2.8024eV), the donor bound excitons (I_2) (2.798eV) and three different acceptor bound excitons (I_1) at 2.7931eV (Na), 2.7923eV (Li) and 2.7829eV (Cu) are observed. The decaytimes are in good agreement with those reported[3,6] and are summarized in tab.I. It is clearly resolved that with increasing binding energy the decay becomes slower. The lifetimes of the (A^0,X)-complexes are independent of the dopand's-concentration within the experimental error of about 20ps, but the free exciton lifetime varys from 15ps to 120ps in correlation with the risetimes of the bound exciton complexes. The risetime of the Cu-related (A^0,X)-complex partly exceeds the free exciton lifetime showing efficient energy transfer between weakly localized bound excitons and the stronger localized Cu-related (A^0,X)-complex.

Discussion

The experimental results show that in the investigated materials even for low impurity concentrations the lifetimes of the free A-exciton are strongly reduced due to impurity correlated recombination channels. Thereby, the formation of bound exciton complexes plays the dominant role. Free exciton lifetimes down to a few ten ps are observed. The subsequent decay of the bound exciton complexes is ultrafast, decaytimes down to some ten ps occur in the widegap II-IV semiconductors, tab.I. The bound exciton decaytimes are constant in the investigated doping range ($\leq 10^{16}cm^{-3}$). Recently, a decrease of the lifetime of the In-related (D^0,X)-complex for In-concentrations around $10^{17}cm^{-3}$ has been reported[14]. In ZnSe an energy transfer between the most delocalized shallow (D^0,X)-complexes and the deep Cu-related acceptor complex is observed.

Two possible recombination processes control the dynamical behaviour of excitons bound to neutral donors or acceptors: the radiative decay and the nonradiative Auger-recombination. The radiative transition probability decreases with increasing localization, whereas the Auger-

tab.I: Experimental (τ_d) and calculated (τ_c) lifetimes and binding energies E_B of bound exciton complexes in ZnO, ZnS, CdS and ZnSe. For the calculation the theory of R&G[9] is used.

	ZnO				ZnS			CdS				ZnSe	
	τ_d (ps)	E_B (meV)	τ_c (ps)		τ_d (ps)	E_B (meV)		τ_d (ps)	E_B (ps)	τ_c (meV)		τ_d (ps)	E_B (meV)	τ_c (ps)
I_3	150	9.7	146				I_2	100	6.1	149	I_2	40	4.5	139
I_4	440	13.0	243											
I_6	350	15.3	309	I_5	150	8.3	I_1	650	17.2	700	I_1^P	100	5.0	164
I_7	420	15.9	326	I_3	285	16.3					I_1^{Na}	280	9.4	422
I_9	600	19.2	433								I_1^{Li}	350	10.2	473
											I_1^{Cu}	1020	19.6	1270

recombination rate increases with increasing localization. As one can see from tab.I our results clearly indicate radiative decay. Obviously, in the direct gap II-IV semiconductors the radiative decay channel dominates.

Rashba and Gurgenishvili[8,9] (R&G) introduced a model explaining the enhanced oscillator strengths of bound excitons compared to those of the free exciton. In their model the gain in oscillator strength is proportional to the ratio of the volume of the center of mass wavefunction of the bound exciton and the volume of a primitive elementar cell. The wavefunction of the bound exciton is derived from effective mass theory considering the interaction with the neutral impurity as delta-function potential whose amplitude is adjusted for the correct binding energy of the complex. Thereby, the giant oscillator strengths of the bound excitons are due to the breakdown of k-conservation and are proportional to the overlapp between the electron and hole wavefunctions. A decrease of overlap with increasing binding energy is caused by the short range binding potential which attracts one charge carrier of the exciton but repels the other one. The lifetimes τ_d are estimated from the following formula:

$$\tau_d = (4.5\ \ ^2 / (n\, f_{ex}))\ (V / (8\, \pi\, a_{BE}^3)) \qquad (1)$$

where is the emitted light wavelength in cm, n is the refractive index, f_{ex} is the oscillator strength of the free exciton and V is the volume of the primitive cell. a_{BE} is the Bohr radius of the bound exciton in the potential of the neutral impurity given by

$$a_{BE} = h / (2\, m_{ex}\, E_B)^{1/2} \qquad (2)$$

m_{ex} is the effective exciton mass and E_B is the binding energy of the exciton-impurity complex. For small binding energies E_B the radiative lifetimes are shorter than the free exciton one.

Taking equation 1 and 2 the lifetimes of the bound exciton complexes can be calculated using known constants of the host material and the observed binding energies. Tab.I gives the calculated lifetimes τ_c together with the experimental values τ_d. The used parameters can be found in[5,3,7], whereby for CdS the effective mass has been replaced[15] by $0.9m_0$. In general, the experimental and the theoretical lifetimes are in good agreement indicating dominating radiative decay of the bound exciton complexes. Remarkable is the excellent agreement obtained for CdS confirming our experimental results in contradiction to earlier ones[7]. Recently, the nonradiative recombination of excitons in CdS has been investigated by means of calometric absorption spectroscopy[16] (CAS). The results demonstrate nonradiative decay channels for the I_1 and the I_2 lines. Unfortunatly, the measurements have not been quantitative, no quantum efficiencies have been calculated. But if one keep in mind that CAS is extremly sensitive and that the I_1+TA absorption leads to a stronger heating than the I_1 absorption (see fig.4 in[16]), the quantum efficiency of the bound excitons in CdS should be quite close to 1.

The investigation of the dynamics of weakly bound excitons can be used to check or even to determine the parameters used by R&G if they are uncertain or even unknown. In fig.5 the lifetimes of the bound exciton complexes in ZnO are presented as function of the binding energy E_B: $\tau \sim (E_B^{3/2})$. As predicted by the theory of R&G for radiative processes the decaytimes are well proportional to $E_B^{3/2}$ prooving its applicability. But, the absolut values predicted are to small, probably due to an uncertain effective exciton mass. From the experimental lifetimes an effective exciton mass of $1.06m_0$ is determined instead of the

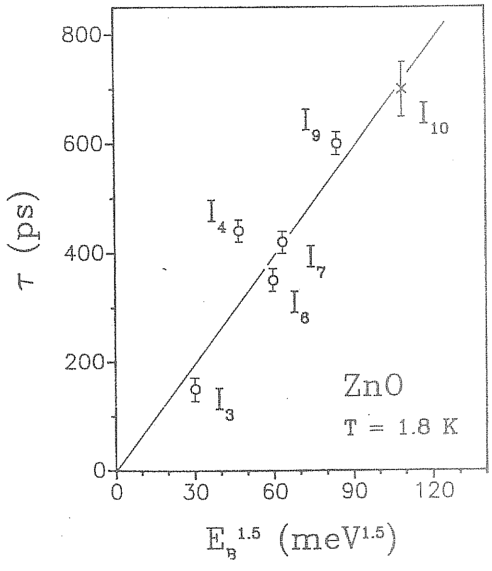

fig.5: Lifetimes τ_d of bound exciton complexes in ZnO in dependence of $E_B^{3/2}$. The data point I_{10} is from ref.[5].

$0.87m_0$ used in the calculation. In ZnS the oscilator strength of the free exciton is still unknown. Using $V=0.0395nm^3$, n-3 and[17] $m_{ex}=0.71m_o$ we obtain $f_{ex}=0.0014$.

Although the theory of R&G gives the general tendency correct, are the deviations sometimes larger than the experimental error, especially for the I_4-line, see fig.5. Despite the fact that the theory of R&G is estonishing powerfull it is simple and neglects a lot of contributions, e.g. correlation effects. Sanders and Chang[18] tried to overcome these shortcomings and also pointed out that for excitons bound to neutral donors the delta-function potential used by R&G should be insufficient. This can be the reason for the deviations observed for the I_4-emission confirming the interpretation as (D^0,X)-complex. Nevertheless, the R&G theory gives good results as far as the exciton binding energy is larger than those of the bound exciton complex. This situation is clearly given in ZnO, ZnS and CdS but not for ZnTe. In ZnTe the Auger-recombination is dominating for larger binding energies[19]. The situatuation is completly changed for deep bound excitons. The exciton bound to an isoelectronic Ni^{2+}-centre in CdS has a binding energy of 362meV much larger than the exciton binding energy. In contrast to the calculated 92ns the complex relaxes within a few picoseconds but exclusively nonradiative[20]. The Ni^{2+}-centre with its electronic d^8-configuration provides extreme efficient nonradiative relaxation channels for the bound exciton due to its multilevel structure.

Summary

Time resolved measurements of not intentionally and weakly doped ZnO, CdS, ZnS and ZnSe crystals are presented. A strong decrease of the free exciton lifetimes down to a few ten ps in connection with an increase of the dopand's concentration is observed. Thereby, a saturation of the impurity correlated recombination channels occur after a delay which depends on the excitation density. Lifetimes of excitons weakly bound to neutral donors or acceptors in the range from 40ps to 1ns are observed in these materials, which are independend of the dopand's concentration. Especially, the rich bound exciton spectrum of ZnO allows a detailed comparison with model calculations revealing a reasonable agreement for radiative decay. We suppose that detailed time resolved investigations in direct gap II-VI semiconductors gives a good possibility to determine or check the effective mass or the oscillator strength of the free exciton. In the investigated semiconductors the radiative decay dominates the Auger-recombination.

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