

Picosecond recombination dynamics at Ni-centres in ZnS and CdS

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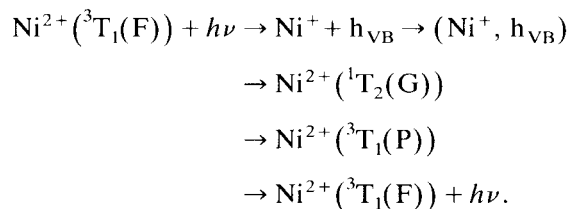
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The internal relaxation processes of the 3d-centre Ni^{2+} and the recombination of photogenerated holes with Ni^+ -centres are investigated by means of time-resolved luminescence spectroscopy of the ${}^3\text{T}_1(\text{P})$ – ${}^3\text{T}_1(\text{F})$ Ni^{2+} transition in ZnS and CdS. The lifetime of the ${}^3\text{T}_1(\text{P})$ state is determined to be 60 ps in ZnS and 400 ps in CdS. Free holes are trapped at Ni^+ -centres forming shallow effective mass like states, average trapping times of 30 ps in ZnS and 50 ps in CdS are observed. The subsequent intracentre relaxation to the luminescent ${}^3\text{T}_1(\text{P})$ -state takes place within a few ps by radiationless cascade processes involving the ${}^1\text{T}_2(\text{G})$ -state.

Deep defects influence the electrical and optical properties of semiconductors. The presence of defects opens additional relaxation channels thus reducing the lifetimes of intrinsic excitations, e.g. excitons or charge carriers. In this paper we present time-resolved detection of the recombination of charge carriers at deep centres. Especially the ${}^3\text{T}_1(\text{P})$ -states of Ni^{2+} -centres in ZnS and CdS have lifetimes in the ps range, which enable us to resolve the formation processes of the ${}^3\text{T}_1(\text{P})$ -state after nonresonant excitation by means of time-resolved luminescence spectroscopy. Therefore, choosing distinct excitation conditions the dynamical behaviour of the excitation channels can be investigated. The excitation mechanisms and their time dependence are discussed.

The incorporation of Ni^{2+} -ions on cation places in ZnS and CdS leads to a variety of localized states in the band gap [1,2], shown as inset of fig. 3 in a “hole” scheme. Most states arise from the 3d-shell of the Ni^{2+} -ions under the action of the predominant T_d crystal field and are located as shown with respect to the $\text{Ni}^{2+}/\text{Ni}^+$ charge transfer process. The state just above the valence

band is an effective-mass-like state introduced by the local potential of the Ni-centre. The ${}^3\text{T}_1(\text{P})$ – ${}^3\text{T}_1(\text{F})$ transition leads to richly structured luminescence bands [3,4] in the near-infrared spectral region and excitation spectra reveal many different absorption processes populating the ${}^3\text{T}_1(\text{P})$ -state [5,6]. The ${}^3\text{T}_1(\text{F})$ – ${}^3\text{T}_1(\text{P})$ absorption shows up as a strong band in the near infrared spectral region, the ${}^3\text{T}_1(\text{F})$ – ${}^1\text{T}_2(\text{G})$ absorption leads to a weak band around 1.9 eV. The charge transfer process as well as band–band absorption excite the luminescence, too. The following recombination cascade after charge transfer excitation can be formulated as indicated in the inset of fig. 3:



All relaxation steps are expected to be radiationless except for the last one leading to the detected luminescence. Two aspects confirm these assumptions. First, both the spin forbidden transition to the ${}^1\text{T}_2(\text{G})$ -state as well as the formation of the shallow effective-mass-like state have only weak oscillator strengths. Second, the energy distances between the excited states are sufficiently

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small for efficient radiationless relaxation by the interaction with optical phonons [7]. Recently, the quantum efficiencies of the $^3T_1(P)$ -states in CdS and ZnS have been determined to 22% and 14%, respectively [8]. In the following, the kinetics of the different excitation steps are investigated by studying the luminescence transients of the $^3T_1(P)$ - $^3T_1(F)$ transition after selective excitation.

The time dependence of the $^3T_1(P)$ - $^3T_1(F)$ luminescence after nonresonant excitation can be approximately described in terms of a simple three-level system. After excitation into the higher excited state the time evolution of the population of the $^3T_1(P)$ -state is given by a sum of two exponential functions with the time constants τ_r and τ_d :

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

τ_r and τ_d are the lifetimes of the excited state and the $^3T_1(P)$ -state, respectively. The shorter one of both lifetimes describes the rise, and the longer one the decay of the luminescence. The transients are fitted by a convolution of the two-exponential decay $I(t)$ with the apparatus response.

The three level solution is valid after excitation via the $^3T_1(F)$ - $^1T_2(G)$ absorption as shown in fig.

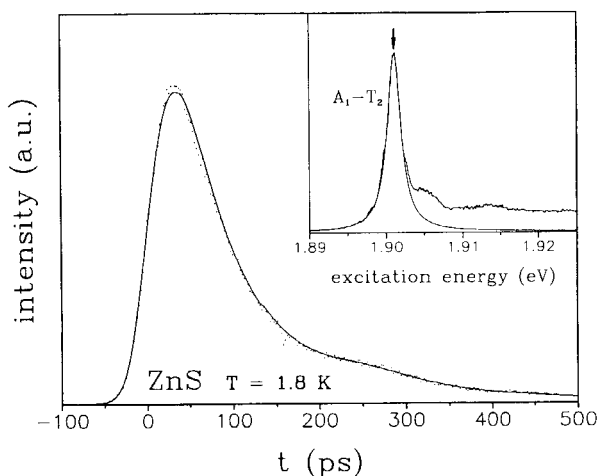


Fig. 1. Transient of the $^3T_1(P)$ - $^3T_1(F)$ luminescence in ZnS at $T = 1.8$ K after excitation via the $^3T_1(F)$ - $^1T_2(G)$ absorption as marked in the excitation spectrum given in the inset.

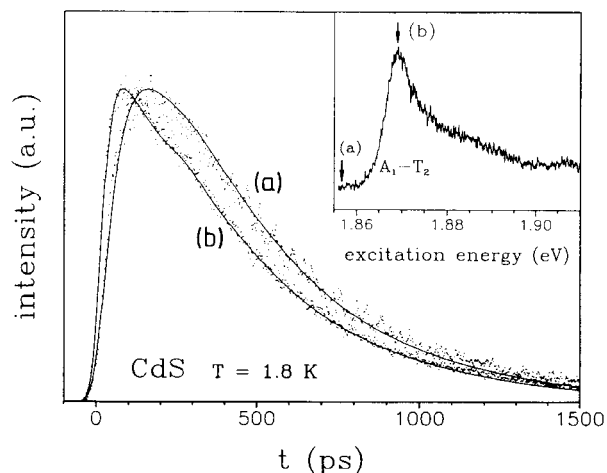


Fig. 2. Transients of the $^3T_1(P)$ - $^3T_1(F)$ luminescence in CdS at $T = 1.8$ K after resonant excitation in the $^3T_1(F)$ - $^1T_2(G)$ absorption (a) and nonresonant excitation (b) as marked in the excitation spectrum given in the inset.

1 for ZnS. The inset represents the excitation spectrum in this spectral region while the main part shows the luminescence transient under excitation into the A_1 - T_2 zero-phonon line (ZPL) at 1.9018 eV as indicated in the inset. A fit of the transient (full line) yields a decay time τ_d of 60 ps, the lifetime of the $^3T_1(P)$ -state, and no resolved rise process. Within the experimental error the risetime τ_r and therefore the lifetime of the $^1T_2(G)$ -state is less than 10 ps. A lower limit is given by the FWHM of the A_1 - T_2 ZPL of 2.2 meV corresponding to 300 fs. The line shape is almost Lorentzian, see the fit in the inset, which implies that the FWHM is determined by lifetime broadening. In CdS the situation is more complex due to the superposition of two different excitation processes. Figure 2 represents in the inset again the excitation spectrum around the $^3T_1(F)$ - $^1T_2(G)$ absorption and now in the main part two luminescence transients recorded under nonresonant (a) (1.8570 eV) and resonant (b) (1.869 eV) excitation as indicated by arrows in the inset. In contrast to ZnS:Ni the luminescence in CdS:Ni can also be excited off-resonance. In CdS the exciting photon energy is sufficient for a two-photon band-band absorption stimulating the luminescence, too. The two transients clearly show

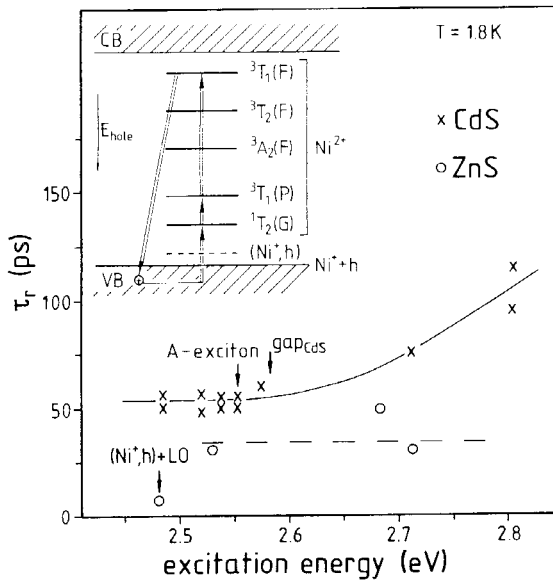


Fig. 3. Rise times τ_r of the ${}^3T_1(P)$ – ${}^3T_1(F)$ Ni^{2+} luminescence for different excitation energies at $T = 1.8\text{ K}$ (circles: ZnS and crosses: CdS). The inset gives the term scheme of Ni^{2+} in CdS in a “hole” picture. The recombination and relaxation cascade following charge transfer excitation is indicated.

the different kinetics of the two excitation channels. Fits of both transients (full lines) reveal the same decay time τ_d of 400 ps, which is identified as the lifetime of the ${}^3T_1(P)$ -state, but different risetimes τ_r . The rise time in the nonresonant case is 60 ps and will be discussed later. The observed rise time of 20 ps for resonant excitation is a result of a superposition of resonant and nonresonant excitation processes. If one subtracts the nonresonant part, estimated from the excitation spectrum, the remaining transient shows no resolvable risetime ($\tau_r < 10$ ps). Obviously, the strong electron–phonon interaction typical for 3d-elements in II–VI semiconductors along with their multiplet termstructure results in efficient radiationless relaxation channels. It is extremely difficult to determine the dynamical behaviour of the ${}^1T_2(G)$ -states directly due to the lack of luminescence and the low oscillator strength.

At higher excitation energies in the region of the charge transfer transition a cascade relaxation process to the ${}^3T_1(P)$ -state takes place, but the intracentre relaxation is sufficiently fast to be

still treated within the three-level approximation. Figure 3 shows the rise times of the luminescence for excitation energies between 2.48 and 2.81 eV for ZnS (circles) and CdS (crosses). At 2.4807 eV the first LO-phonon replica of the shallow acceptor resonance (Ni^+ , h) is excited directly. The rise time of 7 ps lies within the experimental resolution and gives an upper limit for the lifetime of the shallow acceptor ground state. The 30 ps rise time observed above 2.53 eV characterizes the recapture of holes generated in the charge transfer process. The rise time τ_r remains constant over a large energy range indicating that the capture process is not k -selective or that the cooling time of the hot holes is much faster than 30 ps. In CdS below the excitonic band gap the charge transfer process dominates, too, and a risetime τ_r of 50 ps is observed. The hole capture works very efficiently due to the long range Coulomb interaction between the negative effective charge of the Ni^+ centre and the hole, resulting in the possibility to form widely spread effective mass like states [9]. The subsequent relaxation to the ${}^3T_1(P)$ state takes place by radiationless cascade processes.

Above the band gap the charge transfer excitation is suppressed by the band–band absorption. But, as can be seen in fig. 3 for CdS, no distinct change of the rise time is observed near the band edge, only at higher energies the rise time increases. Upon excitation above the excitonic band edge in addition to free carriers excitons are generated which do not participate in the excitation process. Comparative measurements of the A-exciton lifetime and the luminescence rise time τ_r in the same crystal under the same excitation conditions reveal no correlation, which is quite different for shallow impurities [10]. While the A-exciton lifetime of 30 ps increases with the excitation density, the rise time of the Ni^{2+} luminescence remains constant at 90 ps. Further, the continuous development of the rise time in the band-edge region indicates that a similar excitation process is effective above the band edge as below. Nevertheless generated free charge carriers, now electrons and holes, recombine with Ni centres leading to the detected luminescence. Either in addition to Ni^{2+} also Ni^+ centres are

present in the unexcited crystal, or Ni^+ -centres arise by the slow recombination of electrons generated by preceding excitation pulses with Ni^{2+} -centres. The increase of the rise time above the band edge is probably not due to a k -dependence of the capture cross section, since the initial k -vector has no influence in the charge transfer band as stated above for ZnS. But the excited crystal volume becomes smaller with increasing photon energy resulting in a saturation of the Ni-centres within this volume. Further Ni-centres are excited after diffusion of holes out of this region. The Ni-centres are the main recombination channel for holes in the investigated crystals. This interpretation is confirmed by transient (a) in fig. 2 obtained with the homogeneous two-photon band-band excitation. The rise time τ_r of 60 ps is in good agreement with the hole capture time of 50 ps.

The ultrafast luminescence behaviour of a deep impurity is included in a time-resolved investigation to study the kinetics of the excitation processes. The ${}^3\text{T}_1(\text{P})\text{-}{}^3\text{T}_1(\text{F})$ luminescence of Ni^{2+} in ZnS and CdS is found to decay with time constants of 60 and 400 ps, respectively. The fast decay is attributed to a strong admixture of p-like wave functions and competing radiationless processes. The ${}^1\text{T}_2(\text{G})$ states as well as the shallow effective-mass-like states of Ni^{2+} in ZnS and CdS relax within some ps or less to the luminescent

${}^3\text{T}_1(\text{P})$ -state, probably by radiationless cascade processes. The capture of holes by Ni^+ centres takes place within some ten ps. Above the band edge the recombination of free charge carriers with Ni centres is the main excitation channel of the ${}^3\text{T}_1(\text{P})\text{-}{}^3\text{T}_1(\text{F})$ luminescence. An increase of the luminescence risetime occurs if the Ni-centres are saturated in the excited volume of the crystal. Deep impurities are found to be efficient traps for charge carriers whereas shallow impurities are very efficient traps for excitons [10].

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