

# Recombination kinetics of CdS:In

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The luminescence of CdS:In crystals is investigated in the near band gap region by means of time resolved measurements in the ps regime. The changes of the electronic structure induced by the doping give rise to a pronounced decrease of the  $(D^0, X)$  complex lifetime down to 30 ps at some  $10^{17} \text{ cm}^{-3}$ . At higher doping levels, the degeneracy of the conduction band results in radiative band-to-band transitions. The corresponding broad luminescence band decays exponentially within 300 ps. Under high excitation conditions, the recombination rate of band-to-band transitions in heavily doped samples increases strongly. For medium and low dopant concentrations, an increase of the excitation density results in longer decay times due to saturation.

## 1. Introduction

Heavy n-doping drastically changes the electronic structure of semiconductors and as a consequence their luminescence. Due to strong screening of the Coulomb interaction by donor electrons, the binding energy of excitons vanishes and shallow donors are completely ionized. For the highest doping concentrations ( $N_{\text{In}} > 10^{19} \text{ cm}^{-3}$ ), the conduction band of CdS:In is degenerated and partly filled with donor electrons. The luminescence of the crystals near the band gap energy behaves as follows: with increasing but small  $N_{\text{In}}$ , the dominant  $I_2$  emission of donor bound excitons  $(D^0, X)$  asymmetrically broadens and shifts to higher energies. This has already been known for a long time from CdS:Cl samples [1]. At higher  $N_{\text{In}}$ , a single, very broad emission band develops out of the  $I_2$ . Its high energy edge considerably exceeds the band gap energy of unintentionally doped crystals up to several tenth of meV. This emission is caused by non- $k$ -conserving band-to-band transitions [2,3]. The phase transition from excitonic recombination to band-to-band recombination occurs at dopant concentrations of about  $N_{\text{In}} \approx 10^{18} \text{ cm}^{-3}$ .

In 1970, for unintentionally doped CdS, an exponential decay of the  $(D^0, X)$  recombination radiation has been observed with  $\tau = 560 \text{ ps}$  [4]. Newer measurements which make use of a more

straightforward technique reveal  $\tau = 100 \text{ ps}$  [5]. In continuation of earlier work on CdS:In under quasi-stationary excitation with ns pulses [2,3,6], we present here time resolved measurements in the picosecond regime under variation of  $N_{\text{In}}$  as well as the excitation intensity.

## 2. Experimental techniques

The samples were grown by the Frerich–Warminsky vapor-phase method. Indium doping was performed during growth or through annealing of unintentionally doped crystals in an In atmosphere. For the measurements, the samples were immersed in superfluid He at 1.8 K.

A mode-locked Nd-YAG/dye-laser system was used as excitation source. The band gap energy of unintentionally doped CdS is 2.583 eV at 2 K. Therefore, to obtain band-to-band excitation of the samples, the dye-laser was pumped by the frequency-tripled radiation of the Nd-YAG (355 nm, 3.49 eV). The average output power of the dye in the blue spectral region was 60 mW for a repetition rate of 3.8 MHz and a pulse width of about 3 ps. All measurements which are presented here were performed under band-to-band excitation of the crystals at 2.82 eV.

The light emitted from the samples was detected with a 0.75 m monochromator and an

MCP photo-multiplier tube. The response of the system to a short laserpulse ( $\approx 3$  ps) lasts about 50 ps (full width at half maximum).

### 3. Experimental results

In principle, with increasing In concentration  $N_{\text{In}}$ , the decay of the ( $D^0$ , X) complex first becomes faster under low-excitation conditions. Around  $N_{\text{In}} \approx 10^{18} \text{ cm}^{-3}$  this tendency turns back and the decay times increase up to 300 ps at highest doping levels.

Fig. 1 shows the transient intensity behavior of the  $I_2$  line for a crystal which exhibits the fastest decay of all our CdS:In samples. As can be seen from the inset, this crystal emits only a single band in the bound exciton region around 2.55 eV. The decay depends on the energy of detection within this band – the higher the energy the faster the decay. Fitting the experimental data by numerical convolution of a simple exponential decay with the system response to the very short laser pulse (curve labeled “laser” in fig. 1) reveals increasing deviations with increasing  $N_{\text{In}}$ . Thus,

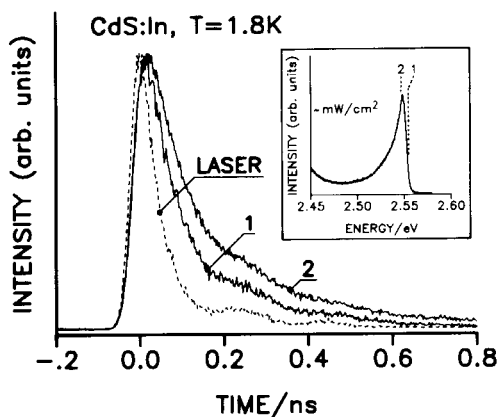


Fig. 1. Luminescence intensity of a doped CdS:In crystal ( $N_{\text{In}}$  some  $10^{17} \text{ cm}^{-3}$ ) in the region of bound exciton emissions  $I_2/I_1$  after band-to-band excitation with weak 3 ps pulses. The inset shows the spontaneous low excitation (Xe lamp) luminescence and two energies of detection labeled “1” and “2”. The excitation energy was  $I_{\text{exc}} = 3.3 \times 10^{-11} \text{ J/pulse}$  at  $E_{\text{phot}} = 2.82 \text{ eV}$ . The dashed curve is the response of the apparatus to the 3 ps laser pulses.

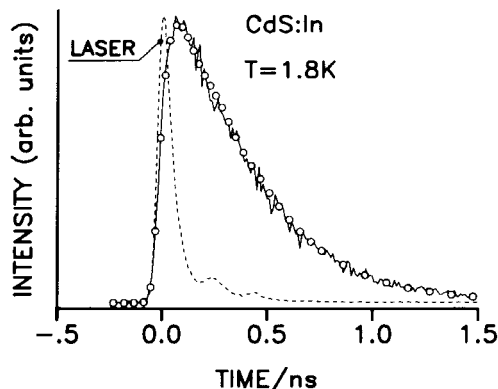


Fig. 2. Luminescence decay of a heavily doped CdS:In crystal ( $N_{\text{In}} \approx 10^{20} \text{ cm}^{-3}$ ). The energy of detection was set to the maximum of the luminescence band (see label “3” in fig. 3). The open circles are the result of a numerical convolution of an exponential decay (300 ps) with the system response to the laser pulse (curve “laser”).  $I_{\text{exc}}$  and  $E_{\text{phot}}$  are the same as in fig. 1.

the decay shown in fig. 1 is not an exponential one, but we can conclude that the decay takes place within about 30 ps for this sample.

Further increase of the In concentration leads to a simple exponential behavior and the time constant increases up to  $\tau = 300 \text{ ps}$  at  $N_{\text{In}} \approx 10^{20} \text{ cm}^{-3}$  (fig. 2). The curve (open circles) which is calculated by the convolution named above fits the experimental data very well. For these crystals,  $\tau$  is independent of the energy of detection over the entire, very broad luminescence band at low excitation intensities.

An increase to high excitation densities changes the transient behavior in different ways, depending on the dopant concentration. For heavily doped samples, the simple exponential decay changes to a faster, more complex one which consists of a fast initial decay followed by the exponential 300 ps decay already found at low excitation density (fig. 3). In this experiment, the energy was  $1.3 \times 10^{-8} \text{ J/pulse}$ , which equals an average power of  $200 \text{ kW/cm}^2$  during the pulse. Additionally, the transients now strongly depend on the energy of detection. The higher the energy, the faster the decay.

In the case of low and medium doping levels the decay in general becomes slower with increas-

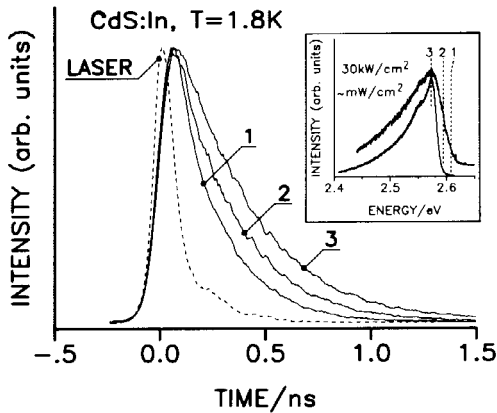


Fig. 3. Luminescence intensity of a heavily doped sample (same as in fig. 2) after intense excitation with  $1.3 \times 10^{-8}$  J/pulse. The inset shows the energies of detection (1, 2, 3) by the use of a low and a high excitation luminescence spectrum. The 30 kW/cm<sup>2</sup> curve was obtained under ns excitation.

ing excitation intensity. This is shown in fig. 4 for the same sample as in fig. 1. In our experiments the occurrence of a narrow-band high-excitation (HE) line complicates the transient behavior. The decay at the position of the HE line is much faster than outside of it. Additionally, the rise at energies "1" and "3" is much slower than that of the HE line ("2").

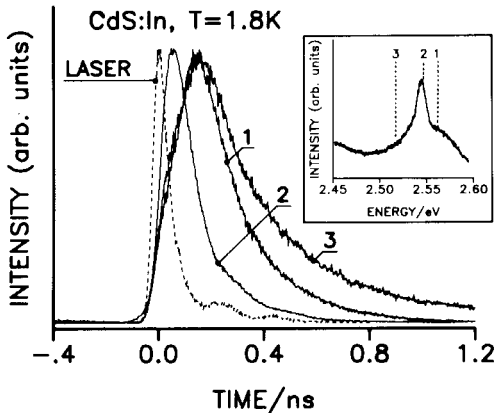


Fig. 4. Transient behavior of the luminescence of a medium doped CdS:In crystal (same as in fig. 1) after intense excitation with  $1.3 \times 10^{-8}$  J/pulse. The corresponding luminescence spectrum exhibits a narrow-band high-excitation line.

## 4. Discussion

### 4.1. Weak excitation conditions

Our measurements reveal decreasing decay times of the I<sub>2</sub> line (100 ps in undoped CdS [5]) with increasing donor concentration. This tendency was already found by Henry and Nassau in 1970 [4]. Beyond that, a continuation of the decrease down to 30 ps is found here for  $N_{In} \approx 10^{18}$  cm<sup>-3</sup>. Assuming an excitonic recombination, the theoretical work of Rashba and Gurgenshvili [7,8] on the oscillator strength of bound excitons yields a simple explanation of this effect. The oscillator strength  $f$  (and therefore the lifetime  $\tau$  of the complex) is connected with the binding energy  $E_{B,exc}$  as follows:

$$f \sim E_{B,exc}^{-3/2} \sim \tau^{-1}. \quad (1)$$

Thus, decreasing binding energies cause decreasing lifetimes of the complexes. But n-doping just decreases  $E_{B,exc}$  due to enhanced screening of the Coulomb interaction by donor electrons. This effect is directly proved by the blue shift of the I<sub>2</sub> line in doped samples [1,9].

The observed decrease of the decay time in one and the same sample by tuning the energy of detection towards higher energies (fig. 1) is caused by inhomogeneous broadening of the emission. Owing to the spatial fluctuations of  $N_{In}$  the binding energy  $E_{B,exc}$  spatially fluctuates, too. Therefore, the higher the energy of recombination radiation, the smaller is  $E_{B,exc}$  and  $\tau$  of the associated complexes. Additionally, complexes with small binding energy can relax into complexes with higher  $E_{B,exc}$ , a process which reduces the lifetime for small  $E_{B,exc}$ . Owing to the considerable homogeneous broadening of the emission line, complexes with different lifetimes contribute to the luminescence at one given energy. This causes the observed deviation from a simple exponential decay with increasing  $N_{In}$ .

At very high dopant concentrations the Coulomb screening length is so small that excitons are no longer stable and shallow donors are ionized. The luminescence is caused by radiative, non- $k$ -conserving band-to-band transitions [3].

Neglecting acceptor states, the recombination rate is proportional to the density of occupied states in the conduction band and the density of empty states in the valence band. With  $n_0$  = concentration of electrons in the conduction band introduced by doping,  $n_{\text{exc}}$  = concentration of optically excited electrons (this quantity equals the concentration of holes in the valence band  $n_h$ ) and  $\alpha_{\text{CV}}$  = recombination coefficient, we get the recombination rate after excitation:

$$\frac{d(n_0 + n_{\text{exc}})}{dt} = \frac{dn_{\text{exc}}}{dt} = -\alpha_{\text{CV}}(n_0 + n_{\text{exc}})n_{\text{exc}}. \quad (2)$$

For heavily doped crystals after weak excitation the inequation  $n_0 \gg n_{\text{exc}}$  holds and it follows that

$$dn_{\text{exc}}/dt = -\alpha_{\text{CV}}n_0n_{\text{exc}}. \quad (3)$$

The solution of this differential equation for  $n_{\text{exc}}$  is a simple exponential decay which is in agreement with the experimental observation (fig. 2). The detected time constant  $\tau$  of 300 ps equals roughly the decay times of the electron–hole plasma in unintentionally doped CdS [10].

#### 4.2. High excitation conditions

Let us continue the discussion first for the heavily doped samples. Under high excitation densities, the inequation  $n_0 \gg n_{\text{exc}}$  does not hold, and it follows from eq. (2) that the recombination rate increases with  $n_{\text{exc}}$  and the *square* of  $n_{\text{exc}}$ . This conclusion of the simple model again fits the experimental observation of a fast initial decay after strong excitation (fig 3.).

The dependence of the transients on the energy of detection in heavily doped, highly excited samples is caused by two effects. As can be seen from the luminescence spectrum in fig. 3, the emission band is broadened and shifts toward higher energies in comparison to weak excitation spectra. This is a consequence of band filling by excited electrons (Burstein effect) and heating of the charge carriers. Both effects cause occupation of conduction band states at higher energies and thus luminescence at higher energies, too. If the detector in a time resolved experiment is adjusted

to the energy labeled “1” or “2” in fig. 3, the luminescence decay is accelerated with respect to “3” by the decay of the Burstein effect as well as the cooling of the charge carriers.

At low and medium dopant concentrations, the luminescence has an excitonic origin and an increase of the excitation density results in slower decays. This behavior is caused by saturation of the occupation of neutral donors by bound excitons. Therefore, the fast relaxation of free into bound excitons is blocked and the excitation energy is stored in a dense gas of free excitons. The lifetime of the excitons is now determined by their *recombination* time, which can reach the free exciton *lifetime* in pure crystals of some nanoseconds [11]. This is the basic mechanism of slowing down the decay. But the transients in fig. 4 exhibit an energy dependence which is connected with the occurrence of a narrow-band line of stimulated emission at high excitation densities. This line is caused by stimulated electron–hole plasma recombinations in doped CdS:In [6]. Therefore, the existence of two competing phases determines the time evolution of the luminescence. Just after the excitation pulse, an EHP is formed exclusively in a thin (some  $\mu\text{m}$ ) surface layer and the corresponding emission is observed. Later on, due to recombination and diffusion, the concentration of charge carriers decreases and a phase transition into a dense exciton gas takes place. Therefore, the HE line decays very fast and the excitonic luminescence builds up.

## 5. Summary

The time resolved measurements reveal a strong dependence of the recombination kinetics of elementary excitations on the dopant concentration. In our opinion, the most striking result is that the doping induced transition from an “excitonic” to a degenerated semiconductor is much more clearly seen in the kinetics than in the time integrated luminescence. With increasing donor concentration, the latter merely exhibits a blue shift and a broadening of the near edge emission. In contrast, the kinetics undergo complex changes

of the energy dependence, of the time constant and of the functional behavior of the decay.

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