

TIME RESOLVED SPECTROSCOPY OF DEEPLY Cu-BOUND EXCITONS IN ZnS

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ABSTRACT

The dynamical behaviour of the copper blue luminescence in ZnS has been investigated by time correlated single photon counting. We studied the influence of temperature, excitation density and high magnetic fields on the temporal behaviour of the zero phonon lines and their phonon sidebands. We explain the luminescence in terms of a three level model and show, that energy transfer processes between deeply copper bound excitons via host lattice phonons play a major role for the behaviour of the blue emission in ZnS:Cu.

INTRODUCTION

It is well known, that in wide - gap II-VI semiconductors Cu - impurities cause different luminescence bands in the visible and infrared spectral region [1,2,3]. One of the most extensively studied luminescence transitions is the copper blue emission in ZnS. Recently, Broser et al. have observed for the first time sharp zero phonon lines ZPL [4] in the blue emission and excitation spectra at low temperatures. The purpose of this work is to investigate the dynamic behaviour of this luminescence in dependence on temperature, excitation intensity and external magnetic fields up to 15 T. This enables us to elucidate the nature of the copper center in ZnS and to understand the processes leading to the blue copper luminescence.

EXPERIMENTAL RESULTS

A typical Cu - blue emission spectrum of ZnS is given in [5,6]. The shape of this band is nearly Gaussian with its maximum at 2.8 eV and a halfwidth of 0.17 eV. In contrast to earlier publications [e.g. 6], a pronounced structure, starting with a weak zero phonon doublet at 2.965 eV, has been observed [4].

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The energy distances between the subsequent peaks of the structured emission correspond to typical host phonon modes in ZnS. The zero phonon doublet C_0^1 and C_0^2 (Fig.1 in ref.4) in emission overlaps with a zero phonon line C_0^1 in the excitation spectrum. Contrary to the emission spectrum, where the phonon wings can be explained by phonon frequencies of the host lattice at different points of the Brillouin zone, the corresponding values within the excitation spectrum are most probably connected to local modes of the copper center.

No zero phonon excitation line C_0^2 occurs at temperatures up to 25 K. This implies, that the temperature behaviour of the excitation spectrum shows no thermalization.

Fig.1 shows the zero phonon emission measured at 2.1 K under various laser excitation intensities. With increasing excitation density the intensity of both lines increases, but the C_0^1 line grows faster than the C_0^2 emission. The intensity ratio of the two lines is reversed with increasing excitation density [5].

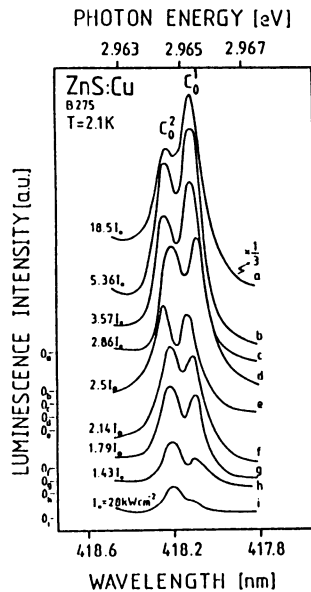


Figure 1: Intensity dependence of the zero phonon doublet on excitation density. With increasing excitation density, the intensity ratio of the two lines is reversed.

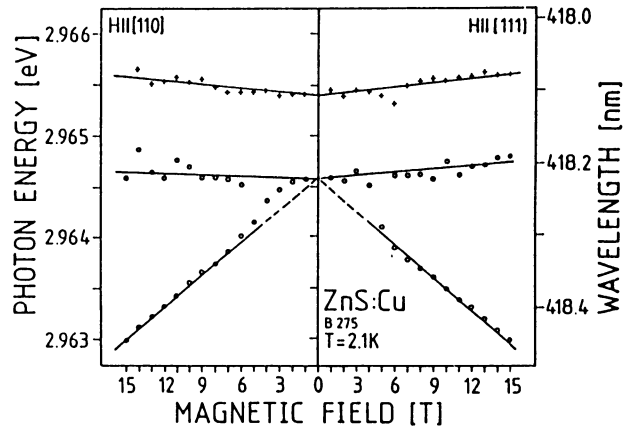


Figure 2: Zeeman pattern of the zero phonon transitions at $T = 2.1$ K for different orientations of the magnetic field. The low energy ZPL C_0^1 splits isotropically into two components with a g -value of about 2.

A similar behaviour can be observed when changing the crystal temperature. At low temperatures, mainly the low energy ZPL is to be seen, while with increasing temperature the high energy ZPL is more pronounced. Both zero phonon lines, however, disappear between 35 - 40 K. In contrast to the behaviour of the spectral lineshape at different excitation densities, an increase of the spectral halfwidth of the two zero phonon transitions at different crystal temperatures could be observed. This indicates, that a thermalization process cannot be the only reason for the change of the intensity relation of the two lines in Fig.1.

The Zeeman measurements (Fig.2) help us to distinguish between the initial and the final state of the luminescence transition.

The low energy ZPL splits isotropically into two components with a g-value of about 2, while the high energy ZPL exhibits no splitting in magnetic fields up to 15 T. As the luminescence intensity of the low energy ZPL increases with increasing magnetic field, the origin of the doublet character must lie in a splitting of the excited state.

The dependence of the ZPL intensity on temperature and excitation density indicates, that the electronic states of the two zero phonon transitions must have different lifetimes. This fact is clearly to be seen in the time delayed emission spectra (Fig.3); 200ns after the excitation pulse, the intensity distribution of the two lines has changed; the high energy component of the zero phonon transition decays faster.

This could also be seen very clearly in recent time resolved experiments in high magnetic fields. The splitting of the ZPL at $B = 11.5$ T leads to an energy separation of $\Delta E = 2.4$ meV between the two lines, which allowed a separate measurement of the decay of both electronic levels. We measured the decay of this high energy component, which is monoexponential over 3 decades of intensity with a smaller time constant than the low energy transition of the ZPL [7].

Fig.4 shows the luminescence decay of the emission maximum of the blue luminescence at 2 and 22 K. At 2 K the luminescence transient shows a multiexponential behaviour. With increasing temperature, the decay seems to become monoexponential. In the beginning of the transient spectrum there is a very short initial process.

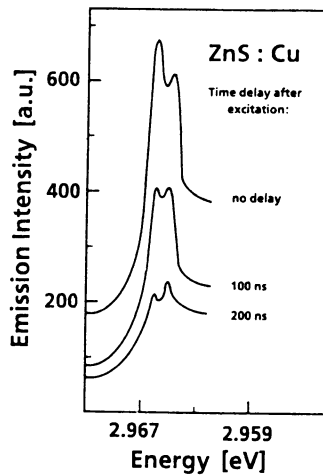


Figure 3: Time delayed emission spectra of the zero phonon emission. The high energy component C_0^1 decays faster than the C_0^2 emission.

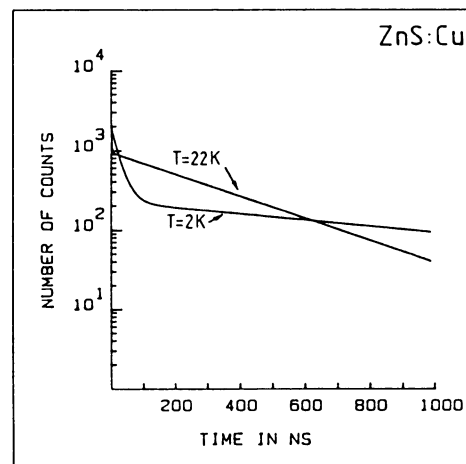


Figure 4: Luminescence transients at the maximum of the copper blue emission. The figure shows the dependence of the decay from temperature. The transient behaviour of the ZPL and the entire blue emission are the same.

DISCUSSION

The behaviour of the two zero phonon lines in respect to crystal temperature, magnetic field, and excitation density underlines the assumption, that both transitions belong to the same luminescence center and that the excited state is split into two electronic levels. The zero phonon transitions take place from these two states to the same final state.

Of the Zeeman pattern, two points are remarkable: The measured g - value is not consistent with that of the Cu^{2+} ion. We also could not measure any dependence of the g - value from crystal orientation, this implies our resumption that a point defect rather than a complex is responsible for the luminescence.

As mentioned earlier in [4], the blue luminescence of ZnS could be described in a model of a deeply Cu - bound exciton. The electronic structure of this bound exciton can be understood with the assumption, that the e - h - exchange interaction is strong enough to split the $J = 1$ state of an exciton, which is bound to an ionized acceptor Cu^+ , into two components. This distinguishes the blue luminescence in ZnS from the corresponding luminescence in ZnO, where Cu^{2+} is the final state [8]. The assumption of an exciton bound to an ionized acceptor might be somewhat unusual. It is known that for a shallow acceptor such a complex is unstable, however, for a deep center the effective mass theory is no longer valid.

The energy model for the observed luminescence transitions is shown in Fig.5., which also shows the splitting of the excited state due to the e-h-exchange interaction and the Zeeman splitting of the low energy component of the ZPL.

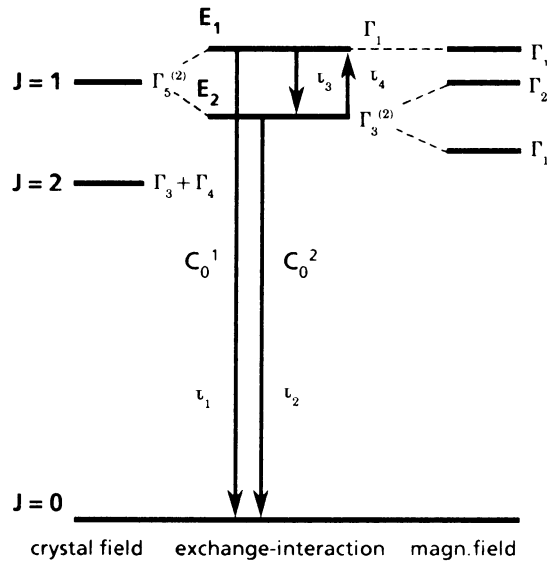


Figure 5: Energy level diagram for the luminescence transitions producing the ZPLs C_0^1 and C_0^2 . τ_1 and τ_2 , respectively, describe the radiative lifetimes of the high and low energy state of the zero phonon transition. τ_3 describes the radiationless relaxation from E_1 to E_2 ($\Delta E = 1 \text{ meV}$) and for τ_4 holds approximately in equ.1,2: $1/\tau_4 = (g/\tau_3)\exp(-\Delta E/kT)$.

The dynamical behaviour of these transitions can be described with the following rate equations, where n_i is the population number of the excited state E_i :

$$\frac{d}{dt}(n_1) = -\frac{1}{\tau_1}n_1 - \frac{1}{\tau_3}n_1 + \frac{1}{\tau_4}n_2 \quad (1)$$

$$\frac{d}{dt}(n_2) = -\frac{1}{\tau_2}n_2 + \frac{1}{\tau_3}n_1 - \frac{1}{\tau_4}n_2 \quad (2)$$

τ_3 depends on the resonant phonon density which is a function of temperature and excitation density. This model fits our measured data for different temperatures well to the decay parameters given in table I. From this results:

- The longest component in the measured luminescence transients describes the radiative lifetime of the low energy state (τ_2).
- The radiationless relaxation (τ_3) is responsible for the fast decay at the beginning of the luminescence process of the high energy component.
- The radiative lifetimes τ_1 and τ_2 are temperature independent, but τ_3 and τ_4 show a strong temperature dependence due to a very effective electron phonon interaction.

Temperature	τ_1	τ_2	τ_3	τ_4
2 K	150 ns	1200 ns	30 ns	3000 ns
5K	150 ns	1200 ns	20 ns	70 ns
10 K	150 ns	1200 ns	3 ns	10 ns
22 K	150 ns	1200 ns	3 ns	4.5 ns

Table I: Decay parameters for the measured luminescence transients at different crystal temperatures. τ_1 and τ_2 are the radiative lifetimes of the excited states E_1 and E_2 , respectively. The time constants τ_3 and τ_4 show a strong temperature dependence, due to the electron phonon interaction and a nonequilibrium phonon concentration during the excitation process. The relation between τ_4 and τ_3 , given in the figure caption of figure 5 is almost obeyed.

At low temperatures, the probability of thermal population of the higher electronic level is small and therefore the time constant τ_4 is responsible for the observed nonexponential behaviour of the luminescence transients.

With increasing temperature, the thermal population of the higher level becomes more probable, i.e. τ_4 becomes much faster. We have to consider the fact, that the temporal halfwidth of the exciting laser pulse was about 3 ns. In the case of a very fast relaxation ($\tau_1, \tau_2 \gg \tau_3, \tau_4$), the measured luminescence transient is more strongly determined by the low energy transition and the decay becomes monoexponential on a nanosecond time scale.

To explain the behaviour of the luminescence in dependence of excitation density, it is not sufficient to take into account a distinct rise of the crystal temperature at higher excitation densities. But during the excitation process, i.e. during the first three nanoseconds, a nonequilibrium phonon concentration can change the probability of relaxation and repopulation to and from the high energy excited state.

The radiationless relaxation and thermal repopulation of the two electronic levels makes it possible to study energy transfer processes: in the case of ZnS:Cu, these processes can be stimulated via acoustical phonons, whereas a similar process, involving optical phonons, could be seen at the copper green luminescence in ZnO [8].

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