CONCENTRATION QUENCHING MECHANISM IN ZnS:Mn

To the memory of my father

CONCENTRATION QUENCHING MECHANISM IN ZnS:Mn

By

MONICA KATIYAR

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AUTHOR: Monica Katiyar , B.Tech. (I.I.T. Kanpur, India)

SUPERVISORS: Dr.A.H.Kitai and Dr.D.T.Cassidy

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ABSTRACT

In this thesis photoluminescence measurements were made on ZnS:Mn thin-films with different concentration of Mn in order to observe the phenomenon of concentration quenching. A mathematical model, based on migration of energy among Mn centres and subsequent transfer to traps, is proposed to explain it. Probability of energy transfer to traps is considered independent of Mn concentration. It is consistent with experimental evidence reported in literature. Using this model we can give physical interpretation to the empirical decay-law for luminescence of Mn centres $n(t)=n(0)\exp[-(t/\jmath)^{\alpha}]$, where $\jmath$ and α change with Mn concentration. We are able to quantify the probability of energy loss to traps using Dexter's equation for dipole-dipole transfer. It is suggested that energy loss to the traps can be influenced by growth technique.

ACKNOWLEDGEMENTS

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CHAPTER 1

Introduction and Present Study

1.1 Introduction

Luminescence in ZnS:Mn at 580 nm is due to transitions among the ionic energy levels of the Mn^{2+} ion sitting in the lattice of ZnS as a substitutional impurity for Zn. Luminescence at 580 nm is due to transition between the first excited state and the ground state and it has been observed in Photoluminescence (PL), Electroluminescence (EL) and Cathodoluminescence (CL) measurements.It is a promising material for solid state display panels. One of the possible ways to improve the performance of these devices would be to increase the concentration of active centres responsible for luminescence, but the concentration quenching phenomenon puts a limitation to it [1,2]. Understanding the mechanism of quenching could be the key to this problem.

Concentration Quenching is a common phenomenon in most of the luminescent materials involving active impurity centres e.g Mn in ZnS, but its mechanism in each case is different. Typically the brightness increases with increasing concentration of active centres untill a critical concentration where it peaks and then it drops suddenly. In ZnS:Mn the critical concentration is ~ 1-2 mole % for PL

measurements. Mn concentration higher than the critical concentration is referred as high concentration and lower than it is referred as low concentration in this thesis. The critical concentration in the case of EL and CL are different. This difference in the EL case has been attributed to more complex excitation processes [3]. Apart from these differences arising due to complex excitation processes the basic mechanism of concentration quenching is expected to be the same. It depends on the nature of interaction between the active centres. Many theoretical models have been proposed in order to understand the mechanism of quenching in ZnS:Mn. This chapter is a review of these models.

1.2 Previous Models

One can divide the existing models in two categories which are discussed below.

1.2.1 Models based on pair/cluster formation

The initial model proposed for interpreting dependence of luminescence efficiency on concentration of active centres in inorganic solids was based on the assumption that only the active centres not having another active centre at any of the nearest z number of sites surrounding it is capable of luminescence. Upon absorption only a certain fraction of the energy goes to the

luminescent centres. Johnson and Williams [4] used this idea to explain the concentration quenching in many phosphors. According to them the efficiency of excitation of luminescent centres, following absorption of the incident energy , is

$$\eta = \frac{\sigma' x'}{\sum_i \sigma^i x^i} \qquad 1.1$$

where σ^i and x^i are the capture cross section and mole fraction respectively of i different type of sites capable of capturing energy. The prime refers to luminescent centres. Now assuming random distribution of luminescent centres, eq(1.1) can be written as

$$\eta = \frac{C(1-C)^Z}{C+(\sigma/\sigma')(1-C)} \qquad 1.2$$

where C is concentration of active centers in fraction, z and σ/σ' are the fitting parameters. This model is successful in explaining concentration quenching in the systems where there is evidence of change in absorption spectra with increasing concentration of active centres. Along with that, the decay constant for emission is the same at all concentrations of active centres. But for the systems like ZnS:Mn that do not fulfil these requirements, other models are invoked.

Warren et al [5] proposed a model in terms of efficiency of emission instead of efficiency of excitation

of active centres. Assuming that z is the number of neighbouring sites that should not be occupied by another active centre for a Mn centre to emit light the dependence of emission intensity on Mn concentration is given by

$$I = K \; C\exp(-zC) \qquad\qquad 1.3$$

where K is the proportionality constant. Fitting the experimental data for ZnS:Mn thin films it is found that z lies between 20 and 40. This means that a Mn centre does not emit at 580 nm if there is another centre within a sphere of 7 Å i.e within a third-nearest-neighbour position. This model has been challenged [3] because it is difficult to get a value of z that will give a good fit to experimental data for intensity vs concentration of Mn. Moreover this model does not relate the decrease in the luminescence efficiency to decrease in the decay-time. Therefore, such a simple model is inadequate to explain the concentration quenching phenomenon.

1.2.2 Models based on decay-time analysis

In all the previous models for concentration quenching the effect of decrease in the decay time of luminescence with increasing concentration is ignored. There have been efforts to solve the problem from this point of view. Many people [6-9] have suggested that decrease in the decay-time is a result of increase in non-radiative de-excitation processes at higher concentrations. Such models

implicitly explain the reduction in luminescent efficiency of Mn centres at high concentration. The main problem in proposing a mechanism for decrease in the decay-time is to explain the increase in non-exponentiality in decay of emission with increasing concentration.

Busse et al [8] conducted time resolved and site selective experiments and came to the conclusion that the decay of Mn centres in ZnS has three exponential components. The decay equation can be written in the following form

$$B(t)=A_1 exp(-t/\tau_1)+A_2 exp(-t/\tau_2)+A_3 exp(-t/\tau_3) \qquad 1.4$$

where the first term arises from isolated Mn ion τ_1=1.8 msec, the second term arises from Mn atoms strongly coupled τ_2=.4-.6 msec and the third term has not been identified and is assumed to arise from less effectively coupled Mn atoms. A_1, A_2 and A_3 are the fraction of Mn atoms in different groups. One of these three components dominates at each concentration. This is the reason for the decrease in the decay-time with concentration as there are going to be more pairs at high concentration. It also explains the non-exponentiality in decay of emission.

Yang et al [9] generalized the model in order to explain their experimental results. They observed that at high concentrations the decay rate is more temperature dependent than at low concentrations. They proposed that the process of decay could be either fast or slow depending on the environment of Mn atom. If τ_i is the observed radiative

decay-time for ith group of atoms, it can be written as

$$\frac{1}{\tau_i} = \frac{1}{\tau_{ir}} + \frac{1}{\tau_{inr}} \qquad 1.5$$

where τ_{ir} and τ_{inr} are the radiative and non-radiative decay-times respectively for the Mn atom in the Ith group. It is assumed to be different for each group. Now, if $L_i(t)$ represents the light emitted from the ith group of Mn^{2+} in a similar environment, then the observed luminescent emission can be described by

$$L(t) = \sum_i L_i(t) = \sum_i \frac{N_i(0)}{\tau_{ir}} \exp(-t/\tau_i) \qquad 1.6$$

where $N_i(0)$ is the number of excited Mn^{2+} ions in the ith group at t=0. Such a model explains that the decay of emission is non-exponential because the Mn ions in some groups decay faster than others. It was suggested that the decrease in τ_i arises because at higher concentration τ_{inr} decreases due to rapid energy transfer of energy from site to site among Mn centres and subsequent dissipation to non-radiative centres. This process was considered to be thermally assisted resulting in strong temperature dependence. Based on their experimental results Tournqvist [10] and Benoit et al [11,12] supported the model that excited Mn centres lose their energy via interaction with other unexcited atoms, thereby increasing the probable non-radiative decay at high concentrations. No quantitative

analysis was done using this model.

Goede et al [13-15] did EL and PL measurements on ZnS:Mn single crystal and thin films and they observed emission in the red region apart from the yellow emission band at high concentrations. This was consistent with the previous observations [11,16,17]. In order to explain the observed concentration and temperature dependence (at higher temperatures intensity of the red band increase while intensity of the yellow band decreases) of the two bands having the same excitation spectra it was proposed that energy is transferred to the red centres/ non-radiative centres from initially excited Mn centres (yellow centres) via other Mn atoms by a non-radiative energy transfer process. With that assumption, the decay of yellow emission can be described as

$$I(t)=I(0) \ exp \ (-t/\tau_y-t/\tau_{yr}-t/\tau_{yn}) \qquad 1.7$$

where τ_y is the decay-constant for isolated Mn atoms, and τ_{yr} and τ_{yn} are effective decay-constants for energy transfer from a yellow centre to red centre and non-radiative centre respectively. Both τ_{yr} and τ_{yn} are dependent on Mn concentration and this dependence was obtained using curve fitting. It was found that mean energy transfer probability to red centres $\tau_{yr}^{-1} \ \alpha \ C^a$ where a = 1.4 or 1.6. The same will be true for τ_{yn}. This was successful in explaining the temperature dependence of the two bands, but no further information about concentration of the red

centres or non-radiative centres could be obtained. This model does not take care of non-exponentiality in the decay of emission.

To explain non-exponentiality Goede et al [18] used the Yokota-Tanimota diffusion limited relaxation law. According to that the non-radiative energy transfer between the randomly distributed Mn^{2+} ions on the cation sites should be described in a continuum approximation as an energy diffusion process with a diffusion constant D depending on the Mn concentration and temperature. This model leads to the mathematical expression given below.

$$\frac{n(t)}{n(0)} = \exp\left[-\frac{t}{\tau_y} - \sqrt{\pi}\frac{C_n}{C_o}(\frac{t}{\tau_y})^{1/2}\left(\frac{1 + 10.87\ x + 15.5\ x^2}{1+8.743\ x}\right)^{3/4}\right]$$

for $x = D/D_o(t/\tau_y)^{2/3}$ 1.8

where τ_y is the decay-time of an isolated excited Mn^{2+} ion, C_n is the concentration of the non-radiative center, and C_o and D_o are the constant parameters independent of Mn concentration. This expression explains the non-exponentiality in decay-measurements, but to fit it numerically is difficult. There are two unknown parameters C_n and D. The best fit decay curves obtained are for τ_y = 3.3 msec which is larger than the experimentally obtained value between 1.5 and 2.0 msec. Benoit et al [19] show that the Yakoto-Tanimoto expression does not explain the decay

law above 0.5 mole %. Empirically they propose a decay law of the form $n(t)=n(0)\exp[-(t/\tau)^{\alpha}]$ where τ and α change with concentration of Mn.

1.3 Present Study

In this chapter the background of concentration quenching mechanisms in ZnS:Mn is summarized. One can see how starting with the simple assumptions the concentration quenching models became more complex as more experimental information became available. There is still need for a model that can explain both the decrease in decay-time and the increasing non-exponentiality in decay of emission with increasing concentration of Mn and is capable of quantitative estimation. In the present study photoluminescence measurements were done on the thin-films with varying concentration of Mn to observe the emission spectra. Chapter 3 describes the experimental set-up used for this purpose and presents the results. These results are discussed in the light of the proposed model of concentration quenching in Chapter 2 and 4.

Chapter 2 establishes that the physical model of the concentration quenching mechanism involves migration of energy over Mn ions and subsequent transfer to traps based on experimental evidence. In order to put this model in the mathematical form it is required to find out the microscopic processes governing it. It is not possible to observe them individually in the experiments, but mathematical models

based on certain assumptions, to simplify the problem, can be used to fit the experimental data. For the first time a model is proposed in Chapter 4 that enables us to quantify the parameters important to this phenomenon unambiguously. It is also possible to explain the non-exponential behaviour of the decay of emission with respect to time at high concentrations. Chapter 5 concludes by listing the capabilities of the proposed model.

CHAPTER 2

Theoretical Background

The experimental evidence necessary to propose a mechanism for concentration quenching in any system includes identifying energy levels of impurities or defects participating in the process, and interactions and energy transfer processes occurring in the solids. The techniques for determining these are summarized below with the information available for ZnS:Mn.

2.1 Optical Characterization

Spectroscopic information (absorption, emission and excitation spectra) help in identifying the energy levels participating in luminescence phenomena. Other complementary experiments viz. Hall measurements and excitation spectra of photoconductivity (in visible and for shallow levels in the near infra-red) are extremely useful in the determination of energy levels and where they lie with respect to the band-gap of the lattice. Spectroscopy has been a great tool for luminescence studies for ages, but after the advent of lasers and sophisticated detectors it has been possible to get high resolution both in frequency and time domain. It has been very useful in understanding the physics behind

many phenomena.

Using narrow-band lasers site-selective spectroscopy can be utilized to find the difference in optical behaviour of active centres at different sites. Fluorescence-line-narrowing is also used for probing the inhomogeneous profile in solids. If the observations are made with respect to time, it also permits the direct observation of energy migration and spectral dynamics [20].

The energy transfer processes can not be observed microscopically but its ensemble effect can be seen in the decay of luminescence intensity of donors/acceptors with time after pulse excitation. The results are analyzed allowing for possible microscopic energy transfer processes taking place in the material.Thus, basic processes are extrapolated back from simple curve-fitting of the decay of luminescence vs time measurements.This method has been extensively used in understanding the energy transfer processes in solids [21].

Information available from ZnS:Mn system is presented here.

2.1.1 Absorption Spectra

Absorption spectra of ZnS:Mn single crystals [22,23] or thin films [14] show five broad peaks at room temperature (due to interaction between optically active ions with lattice modes [24]). These are attributed to intra-ionic levels of Mn^{2+} ion. A typical absorption spectrum and energy

level diagram for Mn^{2+} ion in the crystal field are given in fig.2.1 and fig.2.2 respectively. Absorption spectra can be explained by the simple crystal field approximation. Three low energy bands are assigned to transitions $^6A_1 \rightarrow {}^4T_1$, $^6A_1 \rightarrow {}^4T_2$, $^6A_1 \rightarrow {}^4E, {}^4A_1$ as shown in the fig.2.2. The two larger energy excitation bands are also tentatively assigned to the next intra-ionic levels. The identification of absorption spectra of an isolated Mn ion is certain because similar spectra for the Mn^{2+} ion is found in the same symmetry group of crystal field in other host materials [22].

Absorption spectra shown in fig.2.1 are for high concentrations of Mn (compared to critical concentration 1-2 mole %) for clarity. Zero phonon lines corresponding to these bands are observed even for very low concentrations [17]. Therefore, it is evident that there is no significant change in absorption spectra with concentration.

McClure [22] and Busse et al [8] did observe zero-phonon lines in absorption spectra corresponding to the Mn pairs at low temperatures. It was found that the fraction of Mn ions as pairs was in approximate agreement with their statistical probability considering random distribution. This leads us to believe that concentration quenching is not the result of changes in active centres due to formation of Mn pairs at high concentrations.

The effect of temperature on absorption spectra is to
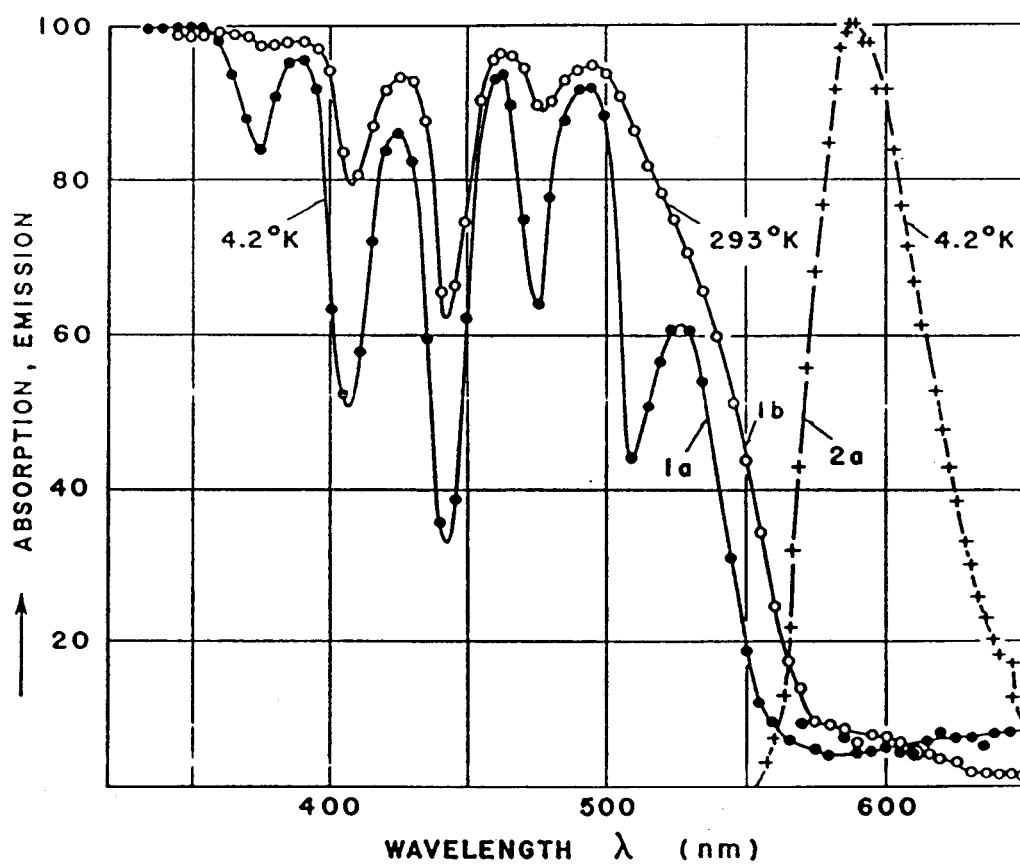
Fig.2.1 Absorption and emission spectra of crystal with 7.3 mole%Mn.Absorption Spectra (1a) 4.2 K (1b) 293 K. Emission spectra (2a) 4.2 K after [23].
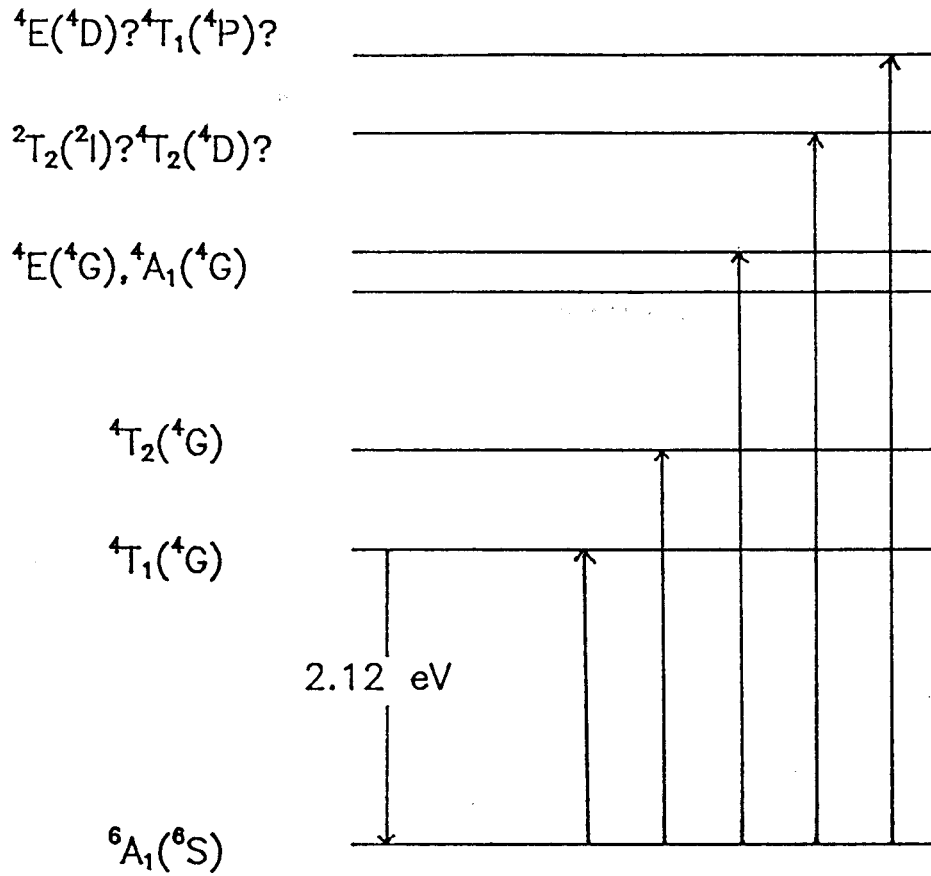
Fig.2.2 Crystal Field split ground and excited states of Mn^{2+} in ZnS; after Gumlich [17].

increase the full width half maxima of the bands at higher temperatures, at high Mn concentrations (fig.2.1).

2.1.2 Emission Spectra

Emission spectra from ZnS single crystals with varying concentration of Mn have been studied by many researchers [13,17]. All of them report a yellow emission band at 580 nm (2.1 eV) for low concentrations of Mn which is attributed to transition between the first excited state and the ground state of the Mn ion. At higher concentrations, emission at 632 (2.0 eV) or 650 nm (1.9 eV) and 763 nm (1.6 eV) have been reported. Fig.2.3 gives the typical emission spectra for different concentrations of Mn. It is interesting to note that the intensity of red emission band increases with temperature at high concentrations. This effect is explained by the model proposed by Yang et al [9] and Goede et al [15] as discussed in sect.1.2.2.

Emission in the red or near infra-red region does not arise from Mn pairs because emission at 560 nm is observed by selectively exciting Mn pairs and recording fast part of the decay spectrum (t< 0.1 msec) [7]. Moreover Gumlich et al [17] argue that decay-time for these centres in the crystal, giving rise to red or near infra-red emission, is larger compared to the decay-time expected from Mn pairs formed at high concentrations. Therefore, it is not possible to simply assign these bands to pair or cluster formation of Mn atoms. Besides, there is no evidence of a corresponding change in
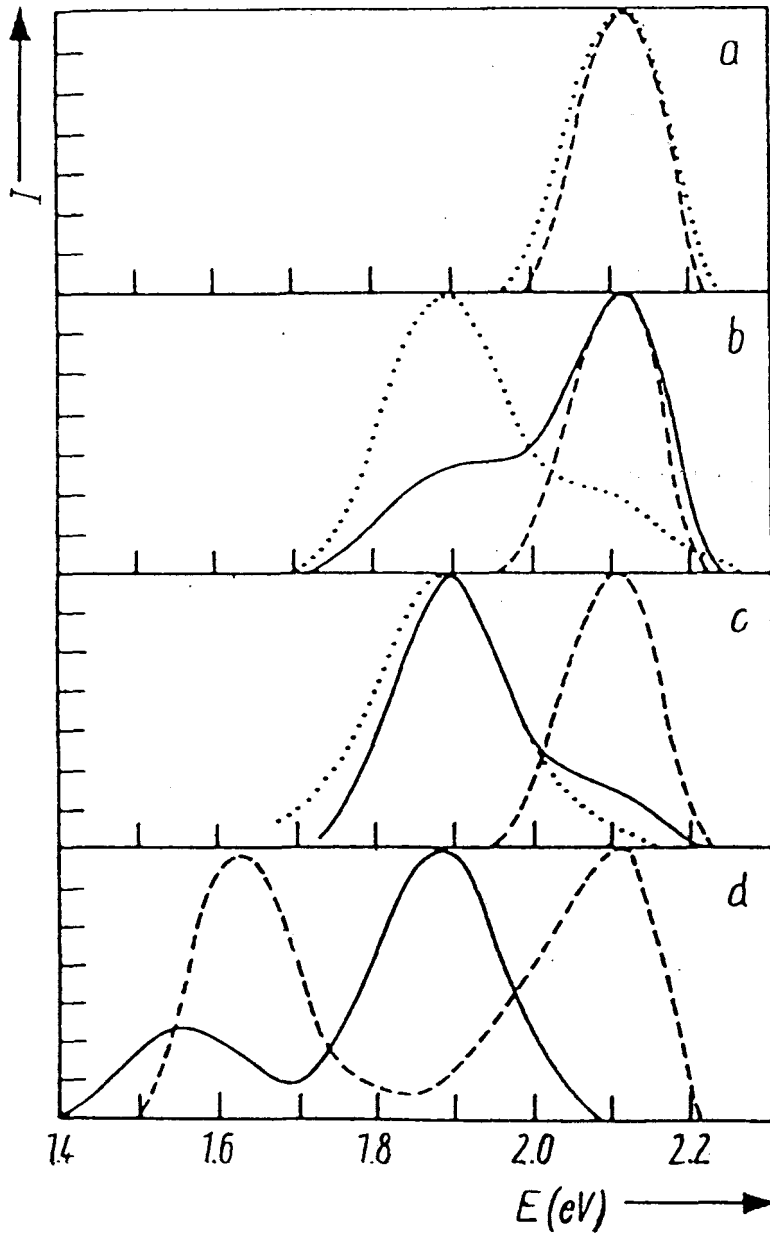
Fig.2.3 Normalized emission spectra of ZnS:Mn single crystal
with Mn concenration a) 1% b) 5% c) 10% d) >10% mole.
488 nm Ar$^+$ laser excitation. T=2 K(----),77 K(————)
and 300 K(......); after [13].

absorption spectra. The origin of the red or near infra-red band is still controversial, but there is enough evidence to believe that it is not related to Mn concentration. This information is used in concentration quenching mechanism proposed in chap.4.

Emission spectra from thin films of ZnS with varying concentrations of Mn have not been studied very extensively using PL to understand the physics of the process. However, PL measurements at 580 nm have been used to characterize thin-films to find out the best annealing conditions [25,26] or compare growth techniques [27]. Emission spectra from ACTFEL devices [11] are similar to the single crystals. Goede et al [14] also confirmed these results by recording emission spectra using PL on the thin films.

2.1.3 Time-resolved Spectroscopy

EL time resolved spectroscopy for a device doped with 7 mole % Mn at 90 K and 300 K after pulse excitation [11] is shown in fig.2.4. This graph clearly shows that the red emission is delayed in time. This supports the theory that red centres are excited via energy transfer from the initially excited yellow centres (isolated Mn ions).

2.1.4 Decay of Emission vs Time Measurements

Decay of emission vs time measurements for the yellow emission band has been recorded [7,9,18,19] and much of effort has gone into explaining its behaviour. At high concentrations the decay rate of yellow emission increases
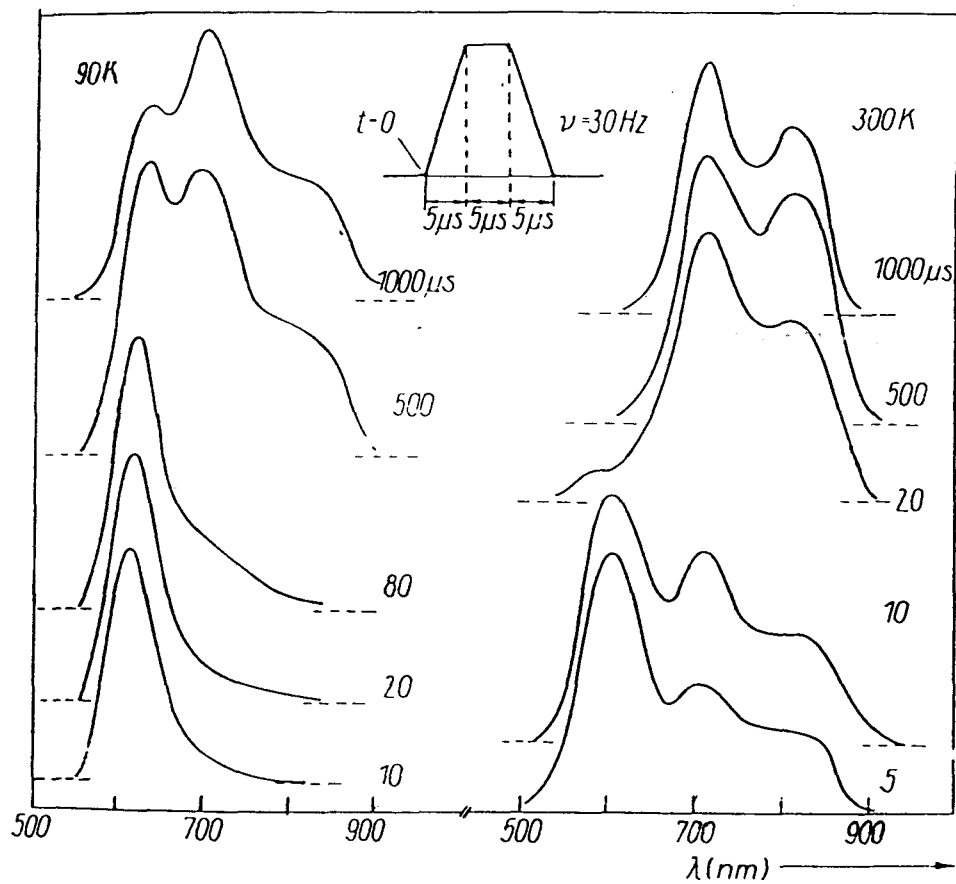
Fig.2.4 EL time resolved spectroscopy for a device doped with 7 mole % Mn at 90 and 300 K. Shape of the pulse excitation is shown; after [11].

and the decay of the emission becomes nonexponential with respect to time (Fig.2.5). Mostly decay-rate is characterized by an effective decay-time where the intensity drops to 1/e of its initial value even though the emission is non-exponential. Such measurements have been reported by many people and they show a sudden drop in decay-time as the concentration of Mn is increased beyond a critical concentration [6,15,28]. ZnS can exist in two crystal forms, zinc blende and wurtzite. In both the cases sulphur and zinc atoms are surrounded by four opposite atoms, but in wurtzite sulphur atoms occupy hexagonal closed packed positions and not the cubic closed packed positions as in zinc blende. Most of the commercially produced single crystals and thin-films are mixed-polytypes [29,30]. Depending on the second and third nearest neighbour positions Mn^{2+} ion can go in four different type of sites [17,31]. Decay-times for isolated Mn ion in different environments vary over a range of $\pm$ 20 %. Its average value is anywhere between 1-2 msec [32] as measured for very low concentrations of Mn in ZnS. Decay-time for Mn-pairs in ZnS crystal is 10^{-4} sec [8]. Decay time for red or near infra-red emission is longer than the decay time of Mn pairs [17].

Apart from the decay rate analysis, the shape of the decay-curve can give information about energy transfer processes taking place in the material [21]. This will be
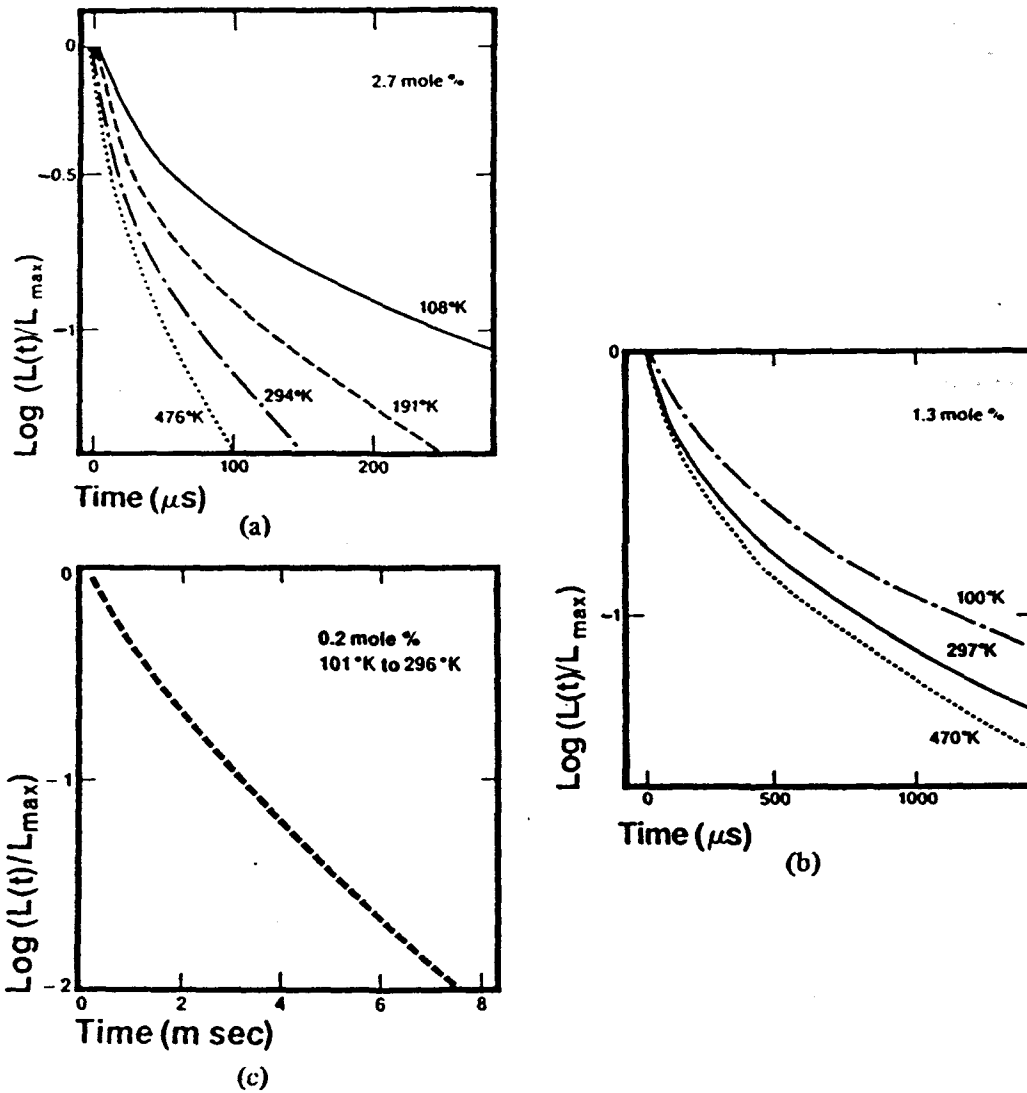
Fig.2.5 Normalized plots of light output vs time following the voltage pulse. The larger decay time at low temperature are probably due to the freezing out of thermally induced non-radiative process; after [9].

discussed in detail in chap.4.

2.2 ODMR/EPR Measurements

Optically Detected Magnetic Resonance and optically influenced Electron Paramagnetic Resonance (EPR) are used to identify the paramagnetic impurity centres and crystal field symmetry around them. These measurements are considered very reliable in identifying the impurity centres, their pairs, and clusters [33]. EPR measurements have been made on the single crystals, powder and thin-films of ZnS:Mn and the results show the existence of isolated Mn atoms and pairs [34]. From EPR measurements on the single crystals it is predicted that Mn in ZnS is distributed randomly. This supports the conclusion drawn from the study of absorption spectra.

2.3 Review of Existing Models

On the basis of all the experimental information available on ZnS:Mn it is possible to review the existing models. Any model based on formation of pairs or cluster is not valid because it will require substantial changes in the absorption spectra and concomitant change in the emission spectra. At the same time this model would predict exponential decay with time.

Models based on varying decay-time of different groups of Mn do not justify the experimental results that show Mn atoms in different sites having approximately the same decay-time. Although pairs of Mn have a smaller decay-

constant their concentration is not enough to explain the concentration quenching [3], considering Mn is distributed randomly (refer to 2.2). At the same time it does not explain the delay in red emission.

A model based on the migration of energy among Mn ions and subsequent transfer to traps in the form of red or near infra-red or non-radiative centres is consistent with experimental evidence. It does not require any significant change in the absorption spectra corresponding to concentration quenching. It explains time delayed sensitized-luminescence of red centres and the effect of temperature on red emission. It is also capable of explaining non-exponential decay of emission, though efforts in that direction have not been very successful in quantitative analysis.

CHAPTER 3

Photoluminescence Measurements

Photoluminescence measurements on thin-films were made in order to observe the emission spectra from ZnS:Mn films with different concentrations of Mn. This chapter gives the details of samples, experimental set-up and results. In view of the concentration-quenching model proposed, these results are analyzed in the next chapter.

3.1 Experimental Set-up

The photoluminescence set-up used for measurements is shown in fig.3.1. The sample is irradiated using the 488 nm wavelength of an air cooled Ar ion laser (American Laser Corporation). The laser power used for excitation was 45 mW. A narrow band-pass filter is used in front of the laser to avoid the detection of other wavelengths coming from the laser. Due to this filter, laser power is reduced by 23 %. Next in the optical path of the beam is the mirror with more than 99 % reflectivity for 480-510 nm. A light chopper (chopping frequency 20 Hz) is placed in the beam for the lock-in amplifier. Lens I (f number=4) is used to focus the beam giving an illuminated area on the sample of ~ 0.25 mm in diameter($1/e^2$). Lens II (f number=2) is used to collimate the scattered light. Lens III (f number=4) is used to focus
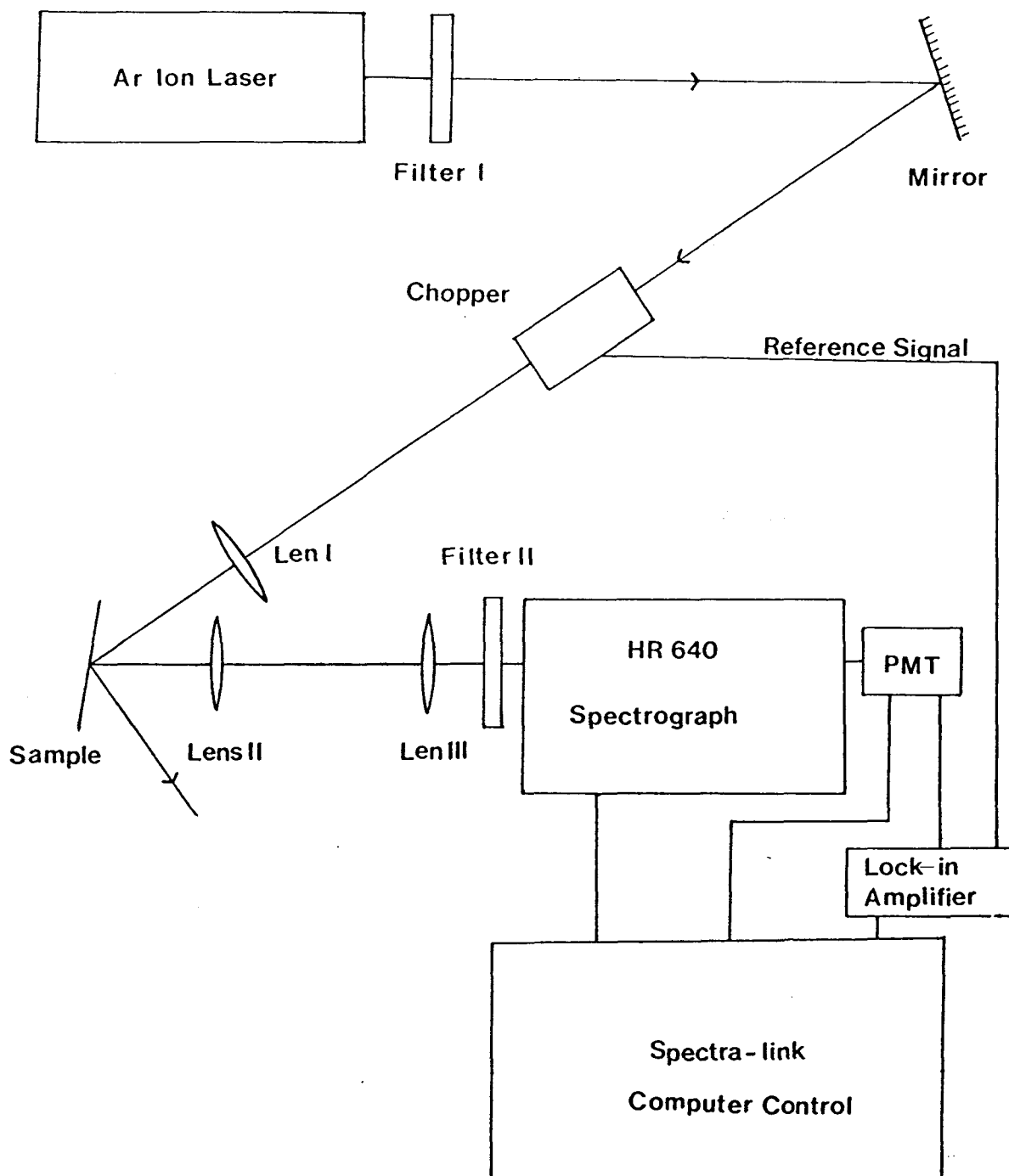
Fig.3.1 Experimental set-up.

spectrometer. Filter II is used to eliminate the scattered light in the spectrometer by preventing the wavelengths below 520 nm from entering it.

Emission spectra were taken using an HR 640 spectrograph system (Instruments SA, Inc.) which was calibrated for the visible spectrum using the known laser wavelengths. Theoretical resolving power of the grating (1200 g/mm) is 0.05 at 580 nm. For slits completely open (1.5 mm) the resolution of the spectrometer was 2 nm at 580 nm. Movement of the grating could be controlled manually or using an external computer through the motor driver module of the spectrograph system.

Data was acquired using an S-1 Photomultiplier tube (Hamamatsu Photonics K.K.) connected to an SR 510 Lock-in amplifier (Stanford Research Systems). The voltage applied across the PMT was 1100 V for all measurements. Due to the low absorption coefficient at 488 nm of the ZnS:Mn sample and small area of illumination, the emitted signal was very small. Therefore, it was necessary to use the lock-in technique to eliminate the noise from the signal. For the same reason, the PMT was water cooled using a thermoelectric cooler (Products for Research,Inc.) that brings the temperature down to 40°C below the ambient temperature. Data was recorded using a computer through a current to frequency converter module of the spectrograph system. The signal was integrated for one minute for each reading. Recorded spectra

were normalised later using the radiant sensitivity of the photocathode in the spectral range 500-900 nm.

Measurements were made in two modes :

(1) Emission spectra were taken from thin-films with different concentrations of Mn using computer control of the spectrometer system.

(2) To observe concentration quenching, emission intensities at 580 nm for different ZnS:Mn samples with varying concentrations of Mn were measured without changing the geometry and other parameters in order to compare the intensities.

3.2 Samples

ZnS thin films used in the experiments were obtained by resistance heated vacuum deposition of ZnS:Mn on silicon substrates [35]. The substrate temperature was about $200^{\circ}C$ and thickness of the films was 190 nm for the first set of films and 180 nm for second set of films. Mn was incorporated in the films by thermal diffusion (at about $400^{\circ}C$) after depositing a thin layer of a known amount of Mn on them. Due to Mn incorporation technique used in preparing the samples Mn concentration is expected to be higher at the surface, but for longer diffusion time (2 hours) Mn concentration profile is quite uniform through out the film (AES in ref [35]).Therefore, we can assume average Mn concentration as characteristic of the films. The average Mn concentration in the films was varied in the range 0.3 mole%

to 44.4 mole %. The chemical compositions of 2.0 mole% and 17.4 mole% samples with estimated error ± 5 % were verified using RBS and was found to be within ± 15 % of the stated value.

3.3 Results

Emission spectra from different samples of ZnS with varying concentrations of Mn were obtained at room temperature. Readings were taken every 2 nm from 500 - 900 nm with slits completely open to maximize the signal. It was not possible to look for finer details of the spectrum. Spectra were drawn with visual aid after taking points with 10 nm resolution. Three typical spectra for low, intermediate and high concentration of Mn are shown in fig.3.2.

At low concentration one can only see the yellow emission band, but at higher concentration a red band with intensity peaking at ~ 720 nm becomes dominant. A ratio of intensity of the yellow band to intensity of the red band (I_y/I_r) is given by the ratio of intensity at 580 nm to the intensity at 700 nm from emission spectra of different samples. A plot of these ratios vs concentration of Mn is shown in fig.3.3. Emission spectra of the sample with 1.1 mole % Mn was recorded from five different points. It was found that I_y/I_r ratio is not constant for a given sample. Error bar in the fig.3.3 gives typical standard deviation from the average value. It is seen that, though there was a
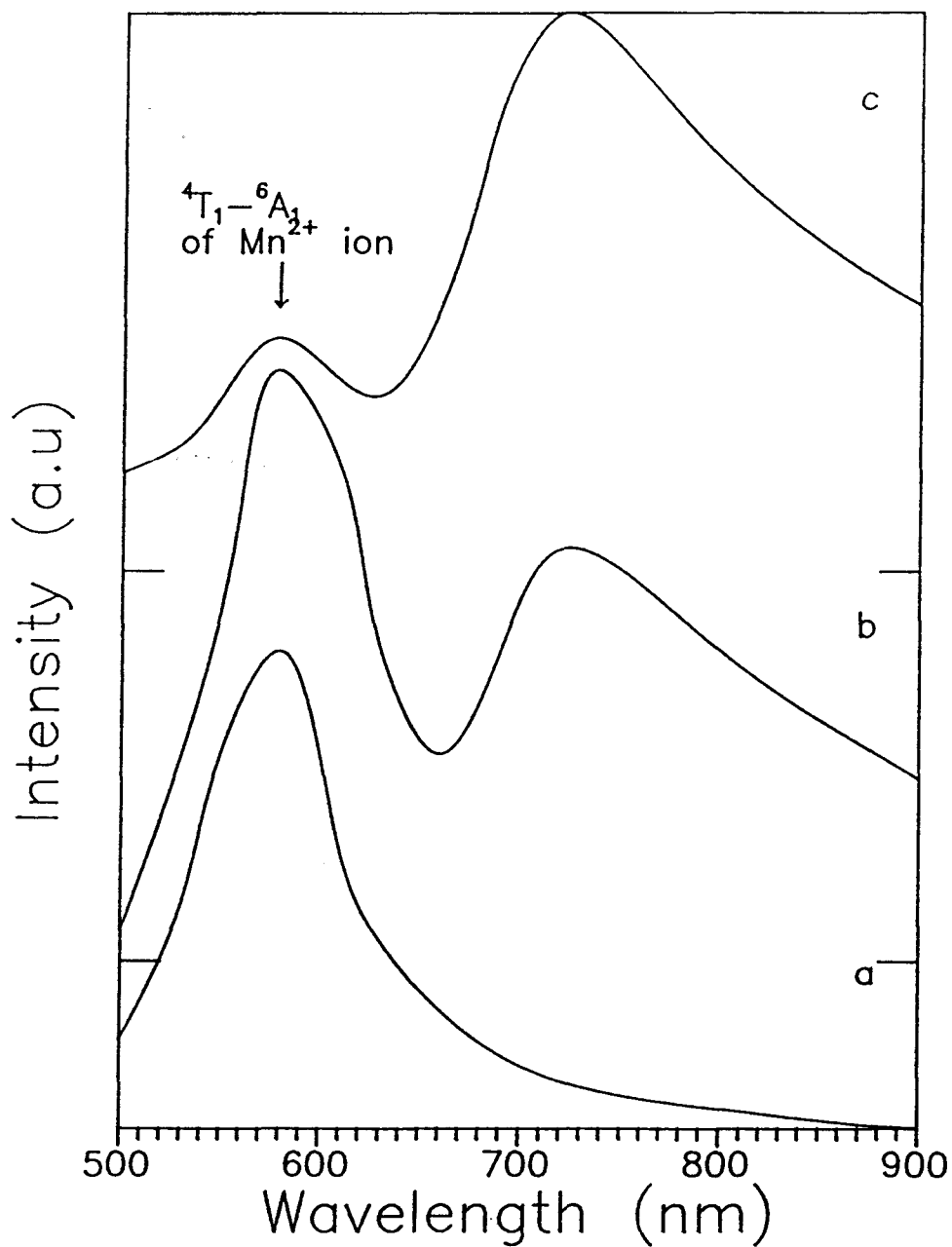
Fig.3.2 Emission spectra from thin-films of Mn concentrations (a) 0.7 mole % (b) 1.6 mole % (c) 19.4 mole %. (488 nm Ar$^+$ excitation.)
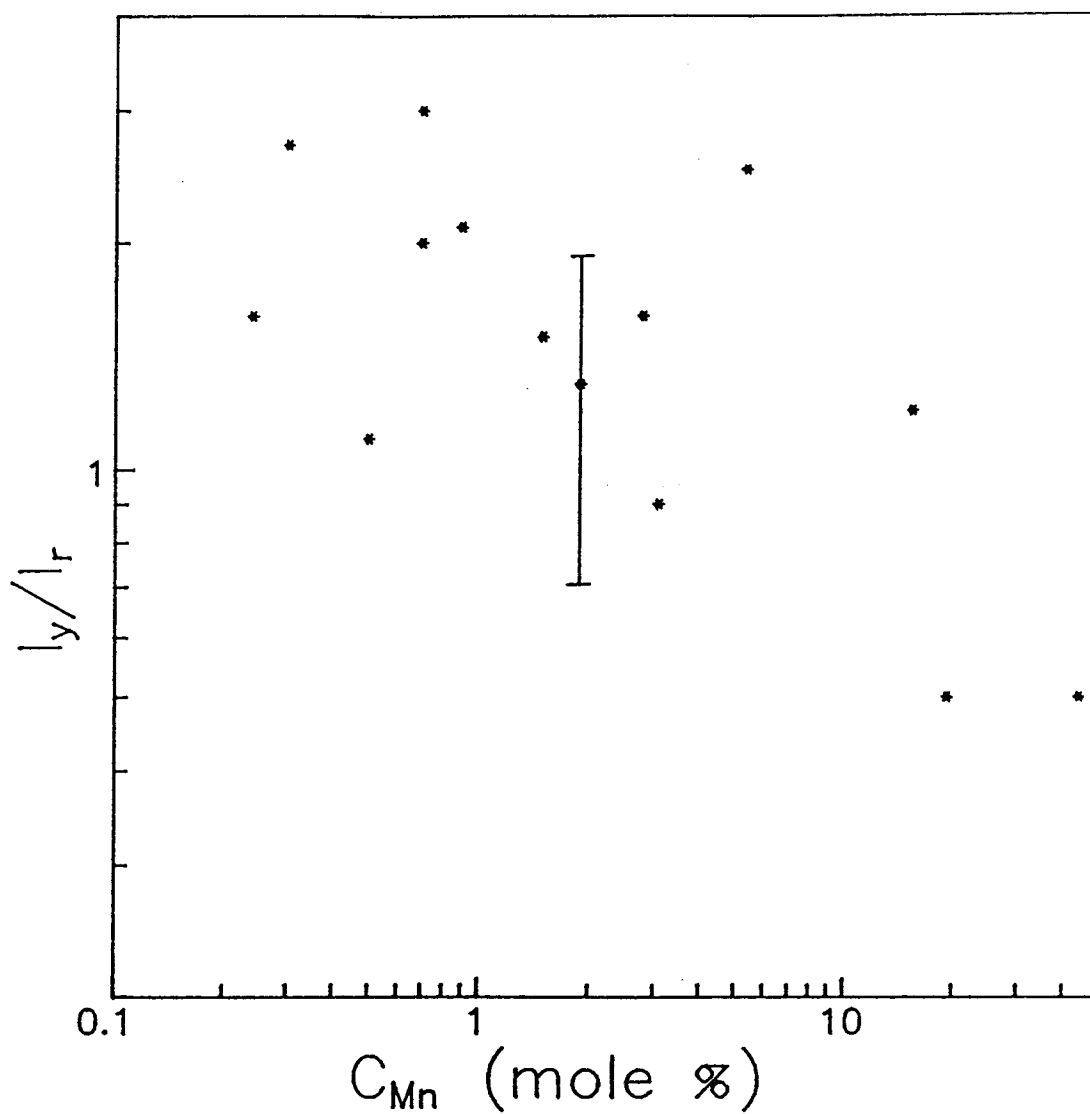
Fig.3.3 I_y/I_r vs Mn concentration plot. The error bar in the figure shows typical standard deviation from the average value in a given sample.
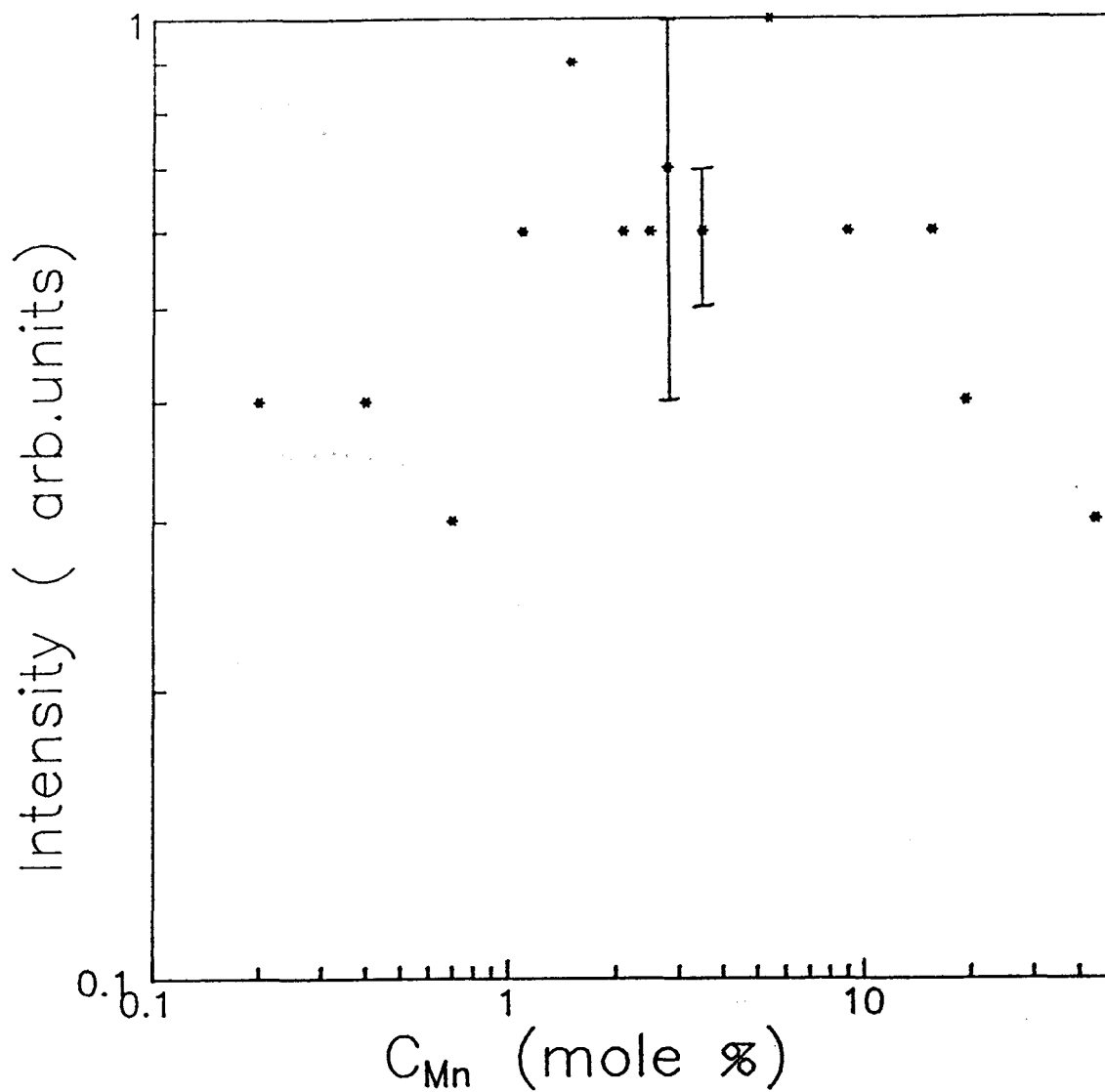
Fig.3.4 Intensity at 580 nm vs Mn concentration plot for the
thin-films of set I. The error bars in the figure show
typical standard deviation from the average value in a
given sample.
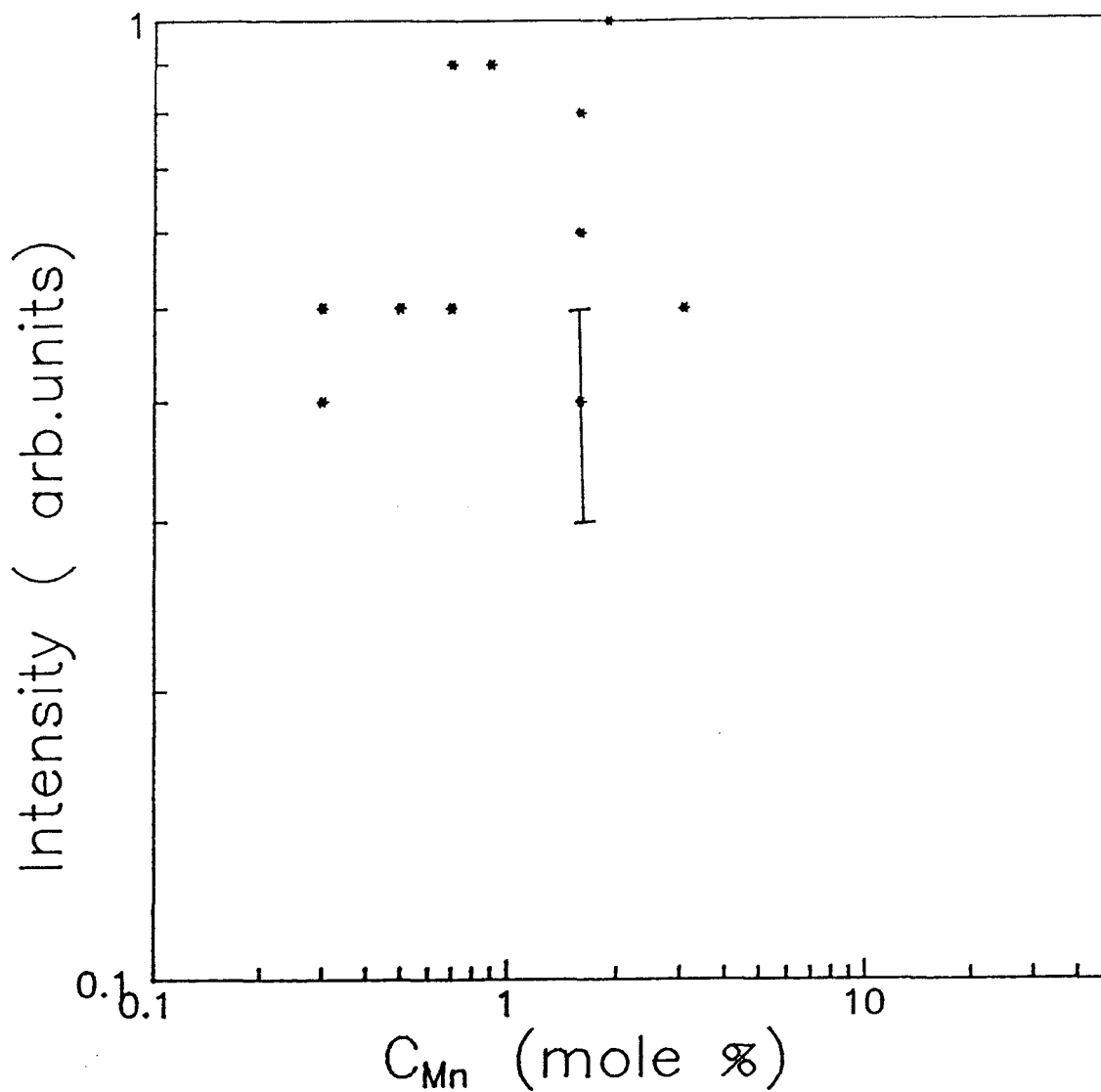
Fig.3.5 Intensity at 580 nm vs Mn concentration plot for the thin-films of set II. The error bar in the figure shows typical standard deviation from the average value in a given sample.

general tendency of increase in red emission at higher concentration, data points are scattered. Some samples with low C_{Mn} give dominant red-emission.

Intensity at 580 nm from different samples were plotted with respect to concentration of Mn for two different sets (fig.3.4 and fig.3.5). In fig.3.4, it is clear that intensity increases with concentration and then drops rapidly. Critical concentration was near 2 mole %. Fig.3.5 shows the similar trend, but there is certain amount of uncertainity due to lack of data at higher concentration. Again samples with approx. the same concentration have very different intensities. This problem has been seen by other experimentalists too [8]. It is very difficult to get the reproducibility of the photoluminescent intensity from samples with same deposition parameter, thermal history and Mn concentration. It may arise due to inhomogeneity in the films as film area is much larger than the illuminated area for photoluminescent measurements. That also explains why in electroluminescence reproducibility is better as the measured light is the integrated emission from the whole area [28]. For the same reason to determine the uniformity of the samples, intensity was measured from fifteen different points on the sample. The error bars in the figures show typical standard deviations from the average value in a given sample.

The next chapter will discuss these results and how

they could be helpful in determining the mechanism of concentration quenching.

CHAPTER 4

Theoretical Model

A new mathematical model of the concentration quenching mechanism in ZnS:Mn, based on the migration of energy among Mn centres and subsequent transfer to traps, is proposed in this chapter.

4.1 Physical Model

The physical picture of the concentration quenching model based on the experimental evidence is discussed in chap.2. Under normal excitation condition, the fraction of excited Mn ions is very low [2,10]. Therefore, one can assume that if a Mn centre is excited it can transfer energy to another unexcited centre through a resonant non-radiative transfer process (refer to 2.1.3). Assuming resonant transfer process is much faster than energy transfer to a red, infra-red or non-radiative centre which will generally be a phonon assisted transfer process due to energy mismatch. This will be true unless such a trap exists very near to a given Mn ion. Therefore, energy will migrate over Mn centres faster until it finds a trap in the form of red, infra-red, or non-radiative centres very near to the energy transfer path. In other words energy loss to a trap
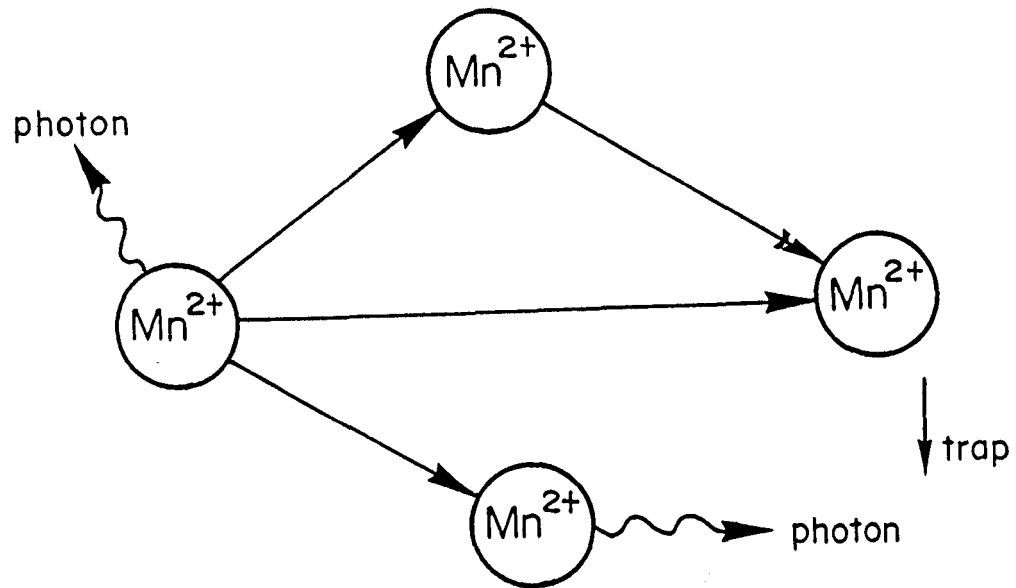
Fig.4.1 Schematic diagram of possible energy transfer paths.

depends on the probability of finding a trap near the path of energy transfer. It is assumed that the concentration of traps is independent of Mn concentration because emission at longer wavelengths is not due to Mn pairs or clusters (refer to 2.1.2). Fig.4.1 depicts this mechanism schematically. This is in contrast to the case where transfer rate to the traps dominates the process instead of migration among Mn centres. For simplicity, traps of various types are not differentiated in the mathematical model. An isolated Mn centre, capable of giving yellow emission, is referred to as a donor. An acceptor is a trap.

4.2 Mathematical model

Total luminescence obtained from the sample is an ensemble average of all the microscopic energy transfer processes described in the previous section. Using statistical analysis one can get decay laws under different approximations. If they explain the shape of experimental decay-time curves, that is evidence that approximations made are correct. Two mathematical models for the problem of concentration quenching are the Diffusion model and the Hopping model.These models are obtained under certain assumptions as discussed here.

Goede et al [18] use the Diffusion model to explain concentration quenching. According to their model, for low concentrations,the decay of emission is non-exponential due to dipole-dipole type interactions between donor and

acceptor sites. At high concentration, diffusion of excitation over donor sites makes energy easily available to traps leading to an exponential decay of emission.Using this model, curve fitting to decay of emission is not possible (refer to chap. 1.2.2). Benoit et al [19] show that the Diffusion model does not explain the decay-law above 0.5 mole %. It predicts that at high concentrations, decay of emission becomes more exponential, which is opposite of what is observed in experiments. This could be due to the fact that the diffusion approximation gives exact solutions for very high concentrations of donors or for very low concentration of donors [36]. It is not the case here, because concentration quenching occurs for ½2 mole% Mn which is neither high enough to assume that energy migration is fast enough to be represented by a diffusion coefficient nor low enough to ignore the migration of energy over donors. According to Golubov and Konobeev [37] using the diffusion approximation for an intermediate case will give results within 15% accuracy. Such an analysis of the decay-law is possible only for ideal conditions.

The Hopping model assumes [20] that number of donors in the sphere of influence of a trap is small. It leads to a non-analytical expression and does not readily lead to conclusive predictions. Another approach to this problem is to use the monte-carlo method [38]. Use of this method may lead to a good fit to decay-time measurements, provided

complete information about the system is given ,(i.e nature
of the traps and their concentration). In the case of ZnS:Mn
we are not certain about the nature of the traps. Therefore,
our aim is to put the concentration quenching model in a
form where it is easy to understand and relate to the
material. To simplify the problem, instead of fitting to the
decay of emission vs time measurements we fit to the
effective decay-time (where the intensity drops to 1/e of
its initial value) vs concentration of Mn. For that purpose
a dynamic theory of energy percolation, described by Blueman
et al [39-41], is used in the context of ZnS:Mn.

When radiative transfer is the only de-excitation
process, the probability that a donor is excited at time t
if it was excited at t=0 can be obtained by the simple
exponential decay-law (assuming all the donors are
identical,independent and have the same probability of
decaying in unit time).

$$n(t)=n(0)\exp[-\frac{t}{\tau_y}]$$ 4.1

where n(0) is the number of donors excited at t=0 and τ_y is
the radiative decay life time of yellow emission. If
migration among donors and subsequent transfer to traps is
taking place as expected in the proposed model, we can write
above equation as

$$n(t)=n(0)\exp[-\frac{t}{\tau_y}]\phi(t)$$ 4.2

where $\phi(t)$ is the probability of energy loss due to transfer

to traps. To calculate it we have to know the microscopic processes occurring. We assume a dipole-dipole type resonant interaction occurring between Mn^{2+} centres. No mechanism is proposed for interaction between Mn centres and traps, because there is very little known about the nature of these traps. We introduce a parameter P_{cap}, i.e. the probability that energy is captured by a trap while it is at any given Mn centre. Physically P_{cap} represents the probability of finding a trap near a Mn centre. Energy transfer to the traps in that case is considered much faster than energy transfer among Mn centres. P_{cap} will be directly proportional to concentration of traps which need not depend on Mn concentration (refer to 2.1.2). Hence, P_{cap} is taken to be constant characteristic of the material.

To get an expression for $\phi(t)$ we will first consider the migration of energy among donors. Microscopic energy transfer rate between donors can be represented in the following form for dipole-dipole interaction [40].

$$\xi(R) = 1/\tau_{tr} \ (d/R)^6 \qquad\qquad 4.3$$

Where d is the next neighbour distance, R is the average distance between Mn atoms and τ_{tr}^{-1} is the rate of transfer to a nearest neighbour donor. Using eq.(4.3) the expression for $\eta(t)$ is obtained by Blueman et al [40], where $\eta(t)$ is the probability of finding a Mn centre still excited at time t if it was excited at t=0 and is interacting with other Mn centres. Taking an ensemble average over all possible

configurations of donor atoms $\eta(t)$ is given by the following expression (see Appendix I)

$$\eta(t) = \exp[- \mu \pi^{3/2} C_{Mn} (\frac{t}{\tau_{tr}})^{1/2}] \qquad 4.4$$

where C_{Mn} is the mole fraction of Mn in ZnS and μ is the proportionality constant depending on the geometry of the host crystal. For ZnS its value is approximately unity. We define the effective time τ_{hop} that energy spends on one Mn centre during the hopping process, by requiring $(\tau_{hop})=e^{-1}$

$$\tau_{hop} = \frac{\tau_{tr}}{[\mu \pi^{3/2} C_{Mn}]^2} \qquad 4.5$$

Until now we have not considered the effect of traps. If there is no energy loss to traps during the random walk of energy, it will not affect the luminescence intensity of donors. In other words $\phi(t)$ will be unity and there will not be any change in the effective decay-time of yellow emission. Unfortunately it is not so and the effect of traps can be included by modifying τ_{hop}, see Appendix II. Now

$$\tau_e = \frac{\tau_{hop}}{P_{cap}} = \frac{A}{C_{Mn}^2} \qquad 4.6$$

where
$$A = \frac{\tau_{tr}}{P_{cap} \mu^2 \pi^3} \qquad 4.7$$

Equation (4.6) shows clearly that in the case of no energy loss to traps (i.e P_{cap} = zero) and τ_e, the effective decay-time for the ensemble loss process, is

infinity. Then, there is no reduction in the apparent decay-constant of yellow emission. On the other hand when P_{cap} is unity, the energy migration model will not hold. In that case, the transfer rate to traps will dominate as stated in the assumptions in the previous section.When losses are present, if $\phi(t)$ is written as $e(-t/\tau_e)$, we obtain from eq.(4.2):

$$n(t)=n(0)\exp(-t/\tau_y-t/\tau_e) \qquad\qquad 4.8$$

Eq.(4.8) explains the decrease in effective decay-time of Mn centres, but it does not exhibit the real time dependence of the decay process. For that purpose, $\phi(t)$ in eq(4.2) can be calculated by considering that transfer probability to a donor multiplied by probability of finding a trap near it, i.e P_{cap}. Using eq.(4.3) transfer rate to a trap is given by

$$\xi'(R)= 1/\tau_{tr}\ (d/R)^6\ P_{cap} \qquad\qquad 4.9$$

Analogous to the previous case of eq.(4.4), we get $\phi(t)$, the probability of energy not being lost to a trap at time t, by taking an ensemble average over all possible configurations of donor atoms. Now eq.(4.2) can be written as

$$n(t)=n(0)\exp\left(-\frac{t}{\tau_y}\right)\exp\left[-\mu\pi^{3/2}C_{Mn}\ P_{cap}^{1/2}\left(\frac{t}{\tau_{tr}}\right)^{1/2}\right] \qquad 4.10$$

In the next section eq .(4.8) and eq.(4.10) are used to explain the experimental data from ZnS:Mn material and estimate the value of P_{cap}.

4.3 Results and Discussion

The model proposed in the previous section does not assume a priori that the concentration of donors near a trap is high as in the Diffusion model. There is one unknown parameter A to be obtained from fitting the experimental data to the model. Determination of this parameter will decide whether there is small or large number of traps near a donor. An advantage of this model is an unambiguous determination of this parameter by simple curve fitting of experimental data of the decay time vs C_{Mn} or intensity vs C_{Mn}. Both methods give consistent results. Apart from that it gives physical interpretation to the empirical decay law for non-exponentiality in the decay of emission suggested by Benoit et al. It is also possible to get a rough estimation of P_{cap} using Dexter's equation for dipole-dipole interaction.

4.3.1 Estimation of A

To estimate the value of A eq. (4.8) gives:

$$\frac{1}{\tau_{app}} = \frac{1}{\tau_y} + \frac{1}{\tau_e} \qquad\qquad 4.11$$

where τ_{app} is the luminescence decay-time to $1/e$ of its initial value. The value of τ_y is known from the decay-constant of yellow emission at very low concentration of Mn. τ_e is given by eq.(4.6).Dependence of the effective decay-time on C_{Mn} is expressed by eq(4.11). It can also be expressed in terms of the brightness vs C_{Mn}. Brightness will

be proportional to C_{Mn} and luminescence efficiency of each centre.It can be represented by the following expression

$$B \propto C_{Mn} \frac{\tau_{app}}{\tau_y} \qquad 4.12$$

Eq. (4.12) explains the characteristic brightness vs C_{Mn} plot. A maximum in brightness will occur at a concentration where $\tau_e = \tau_y$. Beyond this concentration, excitation energy is very mobile and it finds a trap before radiative transition can take place resulting in reduction of brightness. Applying the proposed theoretical model to the experimental results described in Chap.3 one can do curve fitting for intensity vs concentration of Mn data using eq.(4.12). The values of A are 9.0×10^{-7} sec and 1.3×10^{-7} sec for data from set I and set II respectively. Fig.4.2 and fig.4.3 give the best fit curves. It should be noted that fig.4.3 has very high uncertainity (refer to 3.3). Fig.4.4 shows the fit to PL data ($A=5.1 \times 10^{-7}$ sec) for the thin films from Warren et al [25]. It is apparent from the figure that critical concentration is ~ 2 mole%.

Another way of checking the validity of the proposed model is to do the curve fitting to effective decay-time vs C_{Mn} data. Such measurements were not done in this study. Therefore, data from literature is used to test the proposed theory. Fig.4.5 shows the curve-fitting to τ_{app} vs C_{Mn} data for three different sets. The value of A for [15,6,28] are
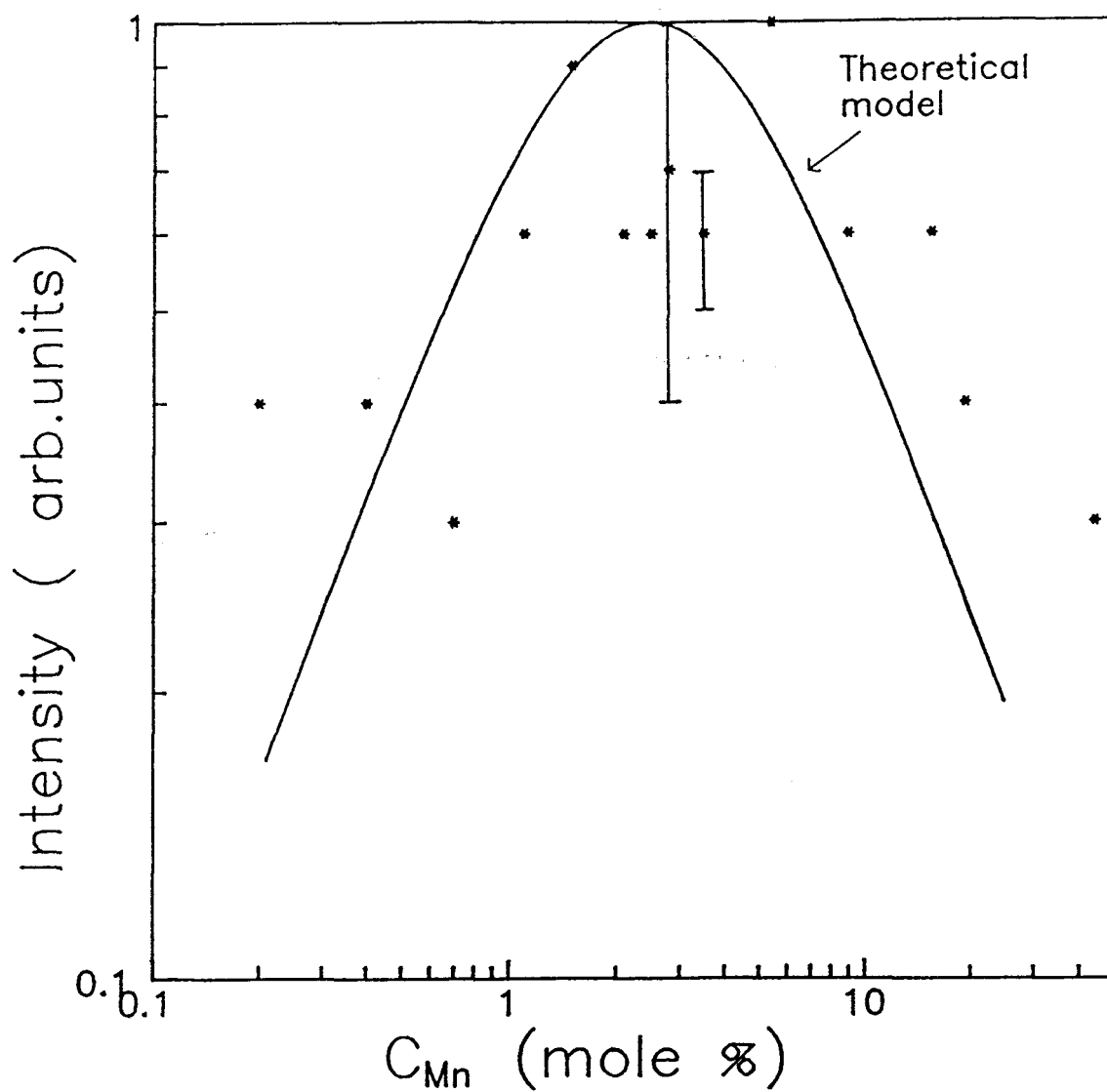
Fig.4.2 Curve fitting to intensity vs Mn concentration data from the set I samples.(A= 9.0×10^{-7} sec)
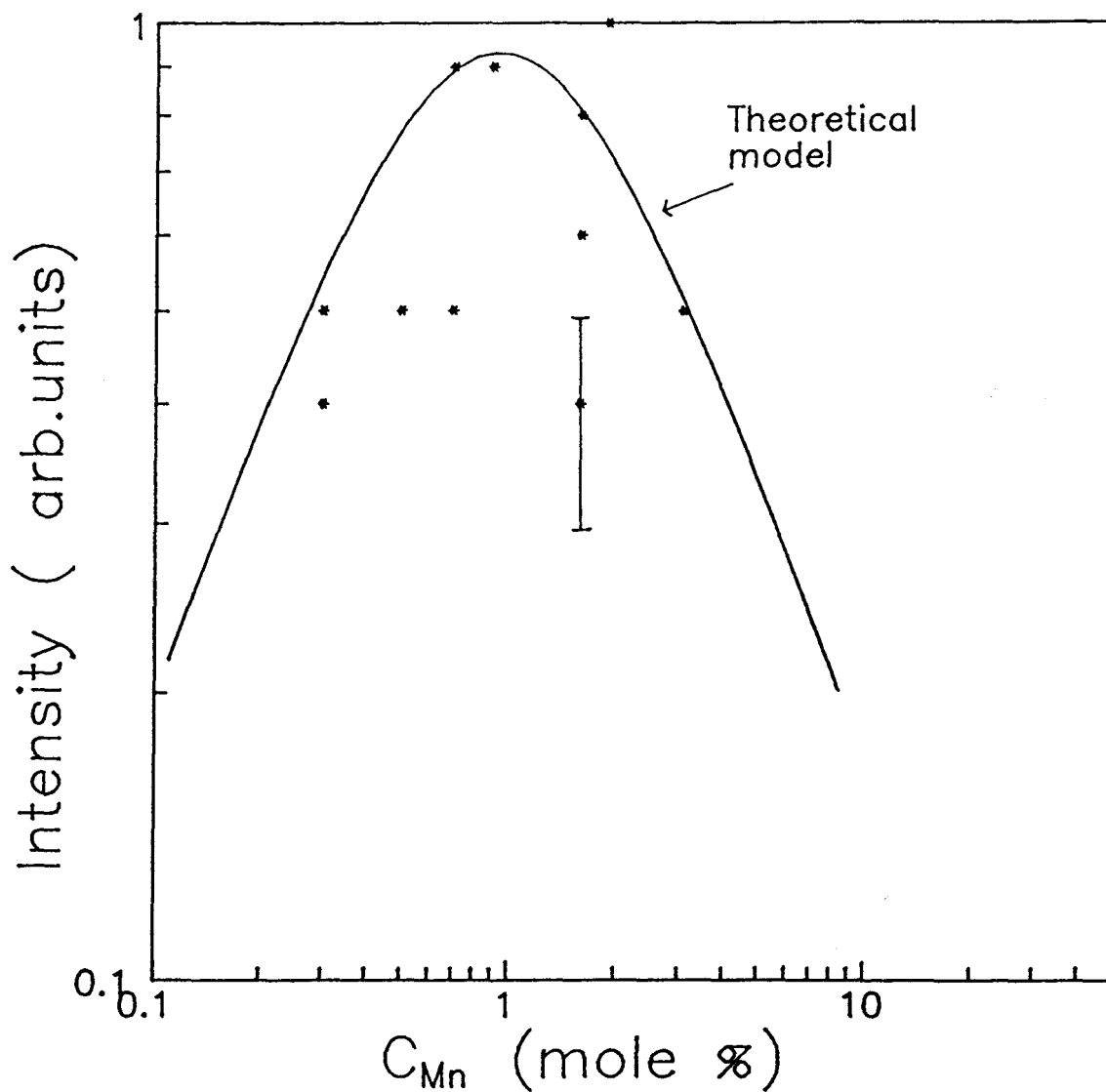
Fig.4.3 Curve fitting to intensity vs Mn concentration data from the set II samples.(A= 1.3×10^{-7} sec)
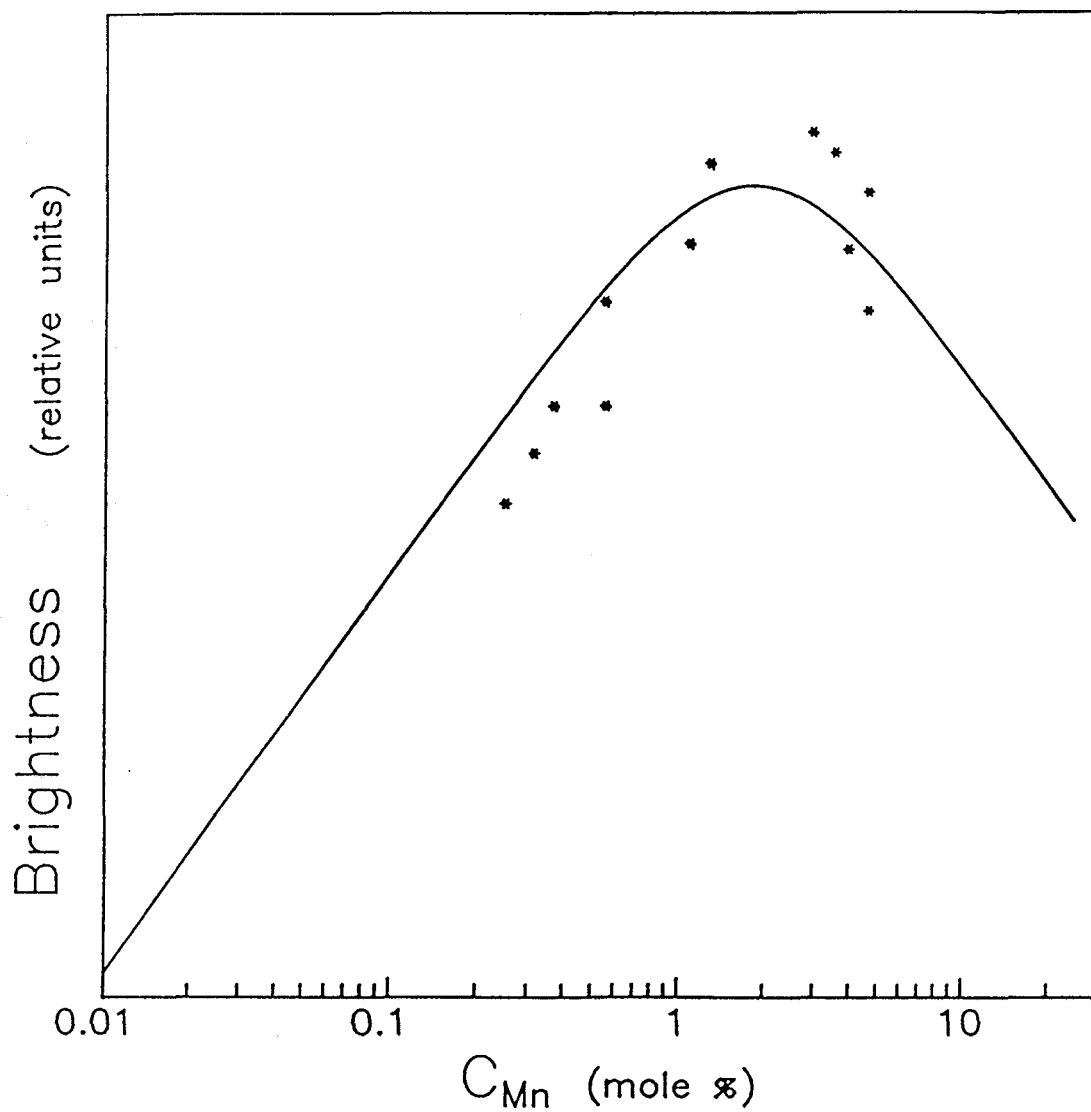
Fig.4.4 Curve fitting to the brightness vs C_{Mn} data on log-log scale from ref [25]. $A=5.1 \times 10^{-7}$ sec for the best fit.
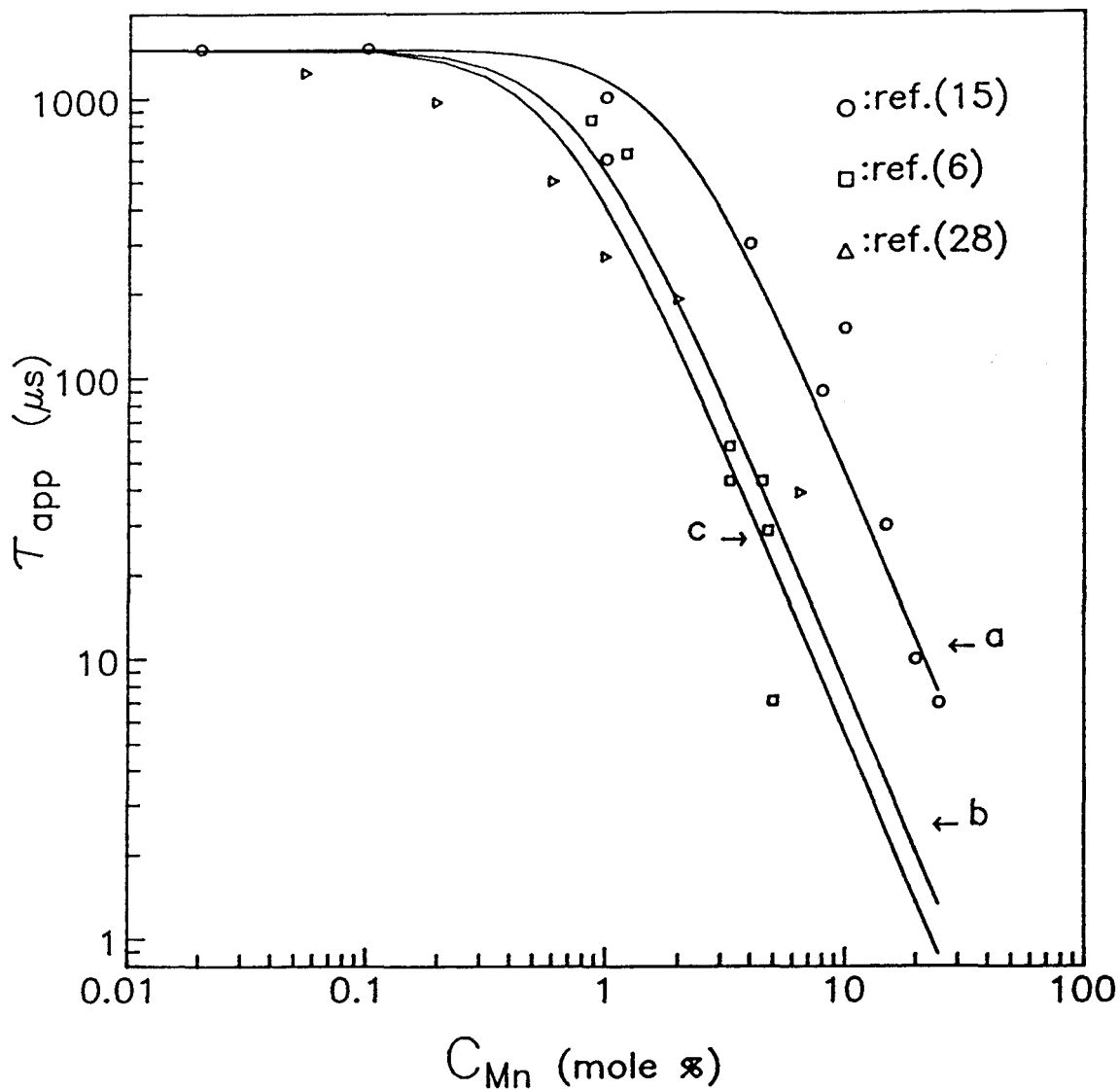
Fig.4.5 Curve fitting to τ_{app} vs C_{Mn} data for three
different sets.(a) A=4.8x10^{-7} sec for ref [15];(b)
0.83x10^{-7} sec for ref [6];(c) 0.55x10^{-7} sec for ref
[28].

4.8×10^{-7}, 0.83×10^{-7} and 0.55×10^{-7} respectively. For these constants fig.4.6 shows the plot of brightness vs C_{Mn} using eq(4.12). Critical concentration for the first case i.e. a single-crystal is ~ 2 mole% and the next two cases i.e. thin-films is ~ 1 mole%. It seems that the value of critical concentration changes in each case.

The parameters that could be different in the two cases are P_{cap} and r_{tr}. Differences in r_{tr} are expected because data for the single crystal is taken at 77 K and the data for the thin-films is taken at 298 K. This would not be very significant. Therefore, it is evident that the probability of loss of energy P_{cap} is different in each case. It is almost six times larger for the thin films compared to the single crystal. That suggests that there are less traps for energy loss in the single crystal. It amounts to doubling the critical concentration for the single crystal. But, it is apparent from fig.4.2 anf fig.4.4 that critical concentration is ~ 2 mole % for the thin-films. It suggests that P_{cap} for the thin films of good quality is comparable to that for the single crystal. The purpose of this analysis was to find out if P_{cap} is dependent on growth technique. It does seem to depend on the way material is grown. This conclusion is supported by experimental results from Migita et al [27]. They report that the films grown by MOCVD with CPM (di-π-cyclopentadienyl manganese) have a higher critical concentration for quenching compared to the films grown by
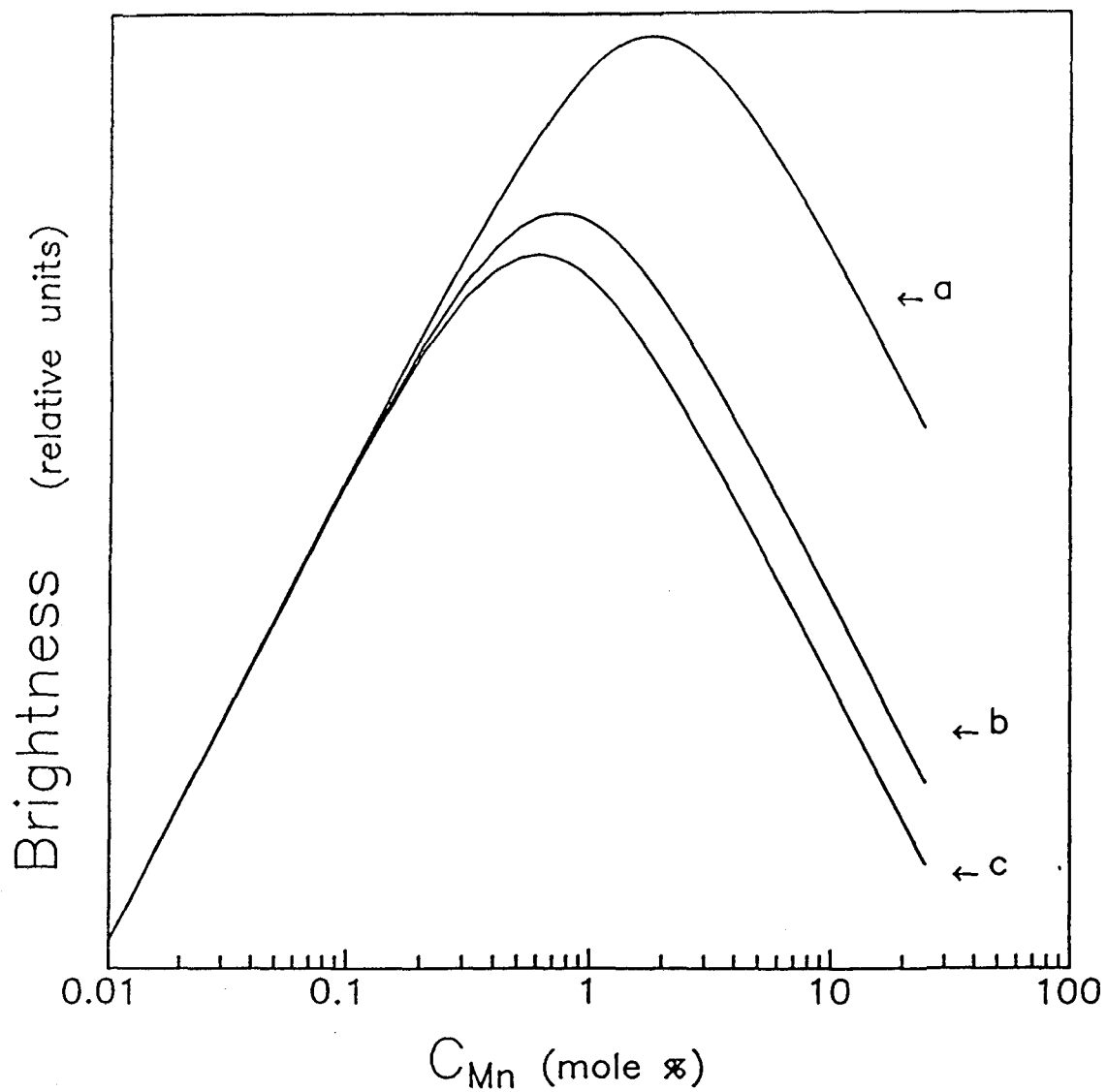
Fig.4.6 Brightness vs C_{Mn} plot on log-log scale

(a)$A=4.8 \times 10^{-7}$ sec; (b) $A=0.83 \times 10^{-7}$ and (c) $A=0.55 \times 10^{-7}$ sec.

Electron Beam Evaporation and MOCVD with TCM (tricarbonyl methylcyclopentadienyl manganese). It might be possible to reduce the value of P_{cap} and increase the critical concentration value by improving the growth techniques.

4.3.2 Non-exponential decay-law

Using eq.(4.10) it is possible to give physical interpretation to the empirical decay-law obtained by Benoit et al [19]. The decay law proposed by them is of the form $n(t)/n(0)=\exp[-(t/\tau)^{\alpha}]$ where α and τ change with Mn concentration. The value of α decreases from 1 to 0.5 as Mn concentration is increased. It is clear from equation (4.10) that at low concentration the first term will be dominant leading to $\alpha=1$. At high concentration the second term will dominate, leading to $\alpha=0.5$. To illustrate this point, best fit to the data for τ_{app} at different concentrations of Mn [15] for single crystal ZnS:Mn gives the value of the constant in eq.(4.6) to be 4.8×10^{-7} sec. Using this constant value in eq.(4.10) we can plot the luminescence intensity with respect to time at different concentrations. Fig.4.7 shows that at high concentrations, the decay law is non-exponential. Unlike the Diffusion model this model does not predict an exponential decay law at high concentrations; instead it predicts that at high concentrations $n(t)/n(0)=\exp[-(t/\tau)^{1/2}]$. This is exactly what is seen by Benoit et al [19]. It is interesting to note that non-exponentiality is more evident in the decay-law at a
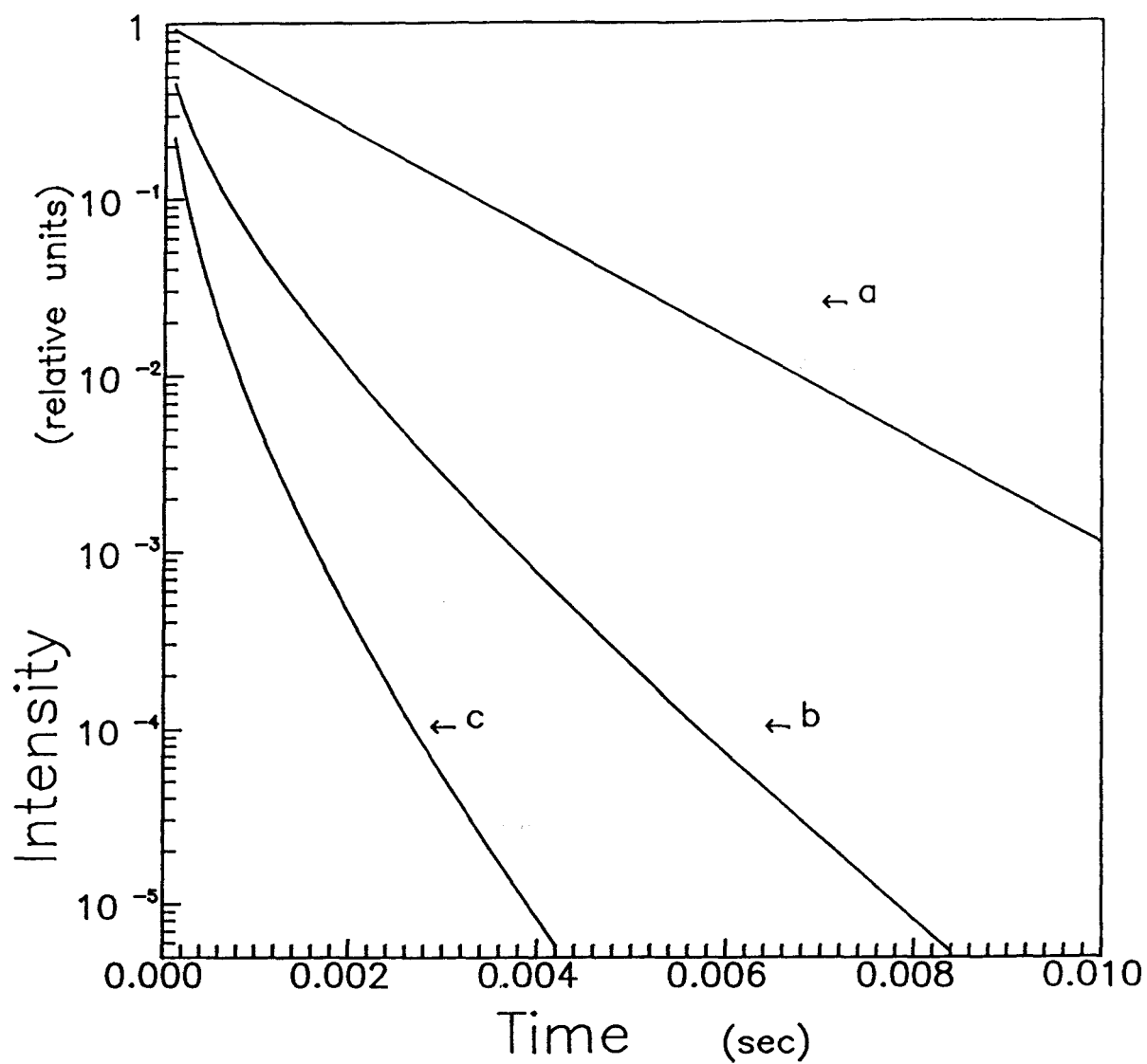
Fig.4.7 Decay of the emission with respect to time for different C_{Mn} (a) 0.1 mole %; (b)5 mole %; (c)10 mole % for $A=4.8 \times 10^{-7}$ sec.

concentration where the effective energy transfer rate to a trap is equal to the radiative transfer rate i.e $\tau_e \sim \tau_y$. In this case, within the radiative life time τ_y of a Mn ion, energy is trapped with a probability of $\sim$ 50 %. As concentration increases, τ_e decreases and the probability of energy reaching a trap increases. Energy transfer to a trap is a non-exponential process with respect to time described by eq.(4.10). Therefore, it is evident that non-exponentiality in the overall decay law is a result of a non-exponential decrease with time in the number of excited Mn ions during the radiative lifetime τ_y.

4.3.3 Estimation of P_{cap}

To go a step further we can estimate P_{cap} by theoretically calculating τ_{tr} from Dexter's equation [42] for dipole-dipole energy-transfer probability.

$$P_{dd} = \frac{3\hbar^4 c^4 Q_a}{4\pi R^6 n^4 \tau_y} \left(\frac{\epsilon}{\kappa^{1/2} \epsilon_c} \right)^4 \int \frac{f_e(E) f_a(E)}{E^4} dE \qquad 4.13$$

where n is refractive index, R is distance between donor and acceptor atom, τ_y is the emission time of isolated Mn ion, $Q_a = \int \sigma(E) dE$ is the area under absorption band, ϵ/ϵ_c is to take into account the dielectric property of the medium, quantity in the integral gives the overlap integral between normalized absorption and emission spectra. Average field strength within the medium is reduced in the ratio $(\epsilon/\epsilon_c)^2 = \kappa$. Therefore, we can set the quantity $(\epsilon/\kappa^{1/2}\epsilon_c)$ equal to unity in the numerical evaluation.

Putting in numerical values in equation (11) r_{tr} , the energy transfer rate between adjacent sites can be estimated. Q_a is $\sim 10^{-16}$ cm^2-eV, n~2.67, overlap integral $\sim 0.01 eV^{-5}$. The overlap integral is calculated using spectra at 4.2 K [23]. We can use this value at high temperature within reasonable approximation. Distance between adjacent Mn centres(R) is 3.8 Å and r_y is 1.5 msec. We obtain r_{tr} to be 10^{-8}-10^{-9} sec. From eq.(4.7) P_{cap} is in the range of 10^{-2} -10^{-3}. This shows that P_{cap} is small, but due to extensive migration among Mn centres, the effective energy loss is very high. If it is possible to learn more about traps in ZnS:Mn, means to reduce the value of P_{cap} might be found.

CHAPTER 5

Conclusions

To summarize the findings of this study, the proposed concentration quenching mechanism has been shown to be consistent with the experimental results reported in the literature. Obtained emission spectra from ZnS:Mn thin-films are in agreement with previous results. The proposed mathematical model has the following advantages over previous models.

(1) It gives the dependence of the intensity of yellow emission and the effective decay-time on concentration of Mn. This correlation is a good fit to the observed behaviour. There is one unknown parameter depending on the physical properties of the system. Therefore, it is possible to get an unambiguous estimation of this parameter.

(2) Using the percolation model it is possible to give physical interpretation to the empirical decay-law suggested by Benoit et al [19].

(3) A quantitative estimation of P_{cap} is possible using Dexter's equation and it turns out to be very small. The value of P_{cap} is dependent on the concentration of traps. Even though the nature of these traps is uncertain, P_{cap} gives an idea about their effect on luminescence efficiency

of Mn centres. It suggests that even though there is very small probability of loss to traps due to one energy transfer step, the over all effect is quite drastic.It seems to depend on growth parameters too. Therefore, it is worth looking into the nature of these traps. Further work is required to investigate the effect of growth parameters on trap concentration.

Coming back to the main incentive of this study,i.e. improving the efficiency of display devices made of ZnS:Mn, the proposed mechanism of concentration quenching leads to two options.

(1) Controlling the concentration of traps in the material.

(2) Preventing migration of energy among Mn ions.

To identify the traps and investigate how they are influenced by growth technique is of academic interest. A very recent work [43] shows the presence of red centres in undoped ZnS films and relates it to the crystallinity of the films. It may be possible to improve the luminescent efficiency by very careful growth techniques, but it may not be practical for manufacturing low cost and large area display devices.

Preventing interaction between Mn ions by selective doping has been suggested [44] and is currently under investigation.

Apart from that there are alternative avenues to explore for the future of display devices. Modification in

the material by incorporating some co-activators, with large absorption cross-section, that can transfer energy to Mn ions is possible [45]. Changes in the device structure to improve the electroluminescent efficiency are also suggested by Chen and Krupka [46]. New materials that can be used as active layers instead of ZnS eg. $AlMg_2O_4$ spinel doped with Mn. Mn^{2+} replaces magnesium in the spinel structure and emits at ~520 nm [47]. Some preliminary work on this material here, at McMaster University, shows that Mn ions do not exhibit concentration quenching phenomenon at a very low concentration. This system is of interest in order to understand more about energy transfer processes in condensed materials. In short the future of luminescent devices is bright, and there is lot of scope for development.

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Appendix I

Consider an excited donor interacting with N randomly distributed donors through n(R) (eq.4.3) and that the density of excited ions is low. This happens to be true for normal excitation in ZnS:Mn. Therefore, the number of unexcited atoms can be approximated the total number of donor atoms. The probability of finding that the atom is still excited at time t is

$$\sigma(t) = \prod_{k=1}^{N} \exp[-tn(R_k)] \qquad \text{A1.1}$$

where it is assumed that the transfer probability is independent, and R_k denotes the actual site of the unexcited donor. Now,

$$\eta(t) = <\sigma> = \lim_{\substack{N \to \infty \\ V \to \infty \\ N/V \to \rho}} \left\{ \int_V \exp[-tn(R)]W_V(R)dV \right\}^N \qquad \text{A1.2}$$

V is the volume over which the integral extends, ρ is the density of donors, and W_V is the probability of finding another unexcited donor at distance R. Assuming a random spatial distribution of donors

$$W_V(R)dV = 4\pi R^2 \frac{dR}{V} \qquad \text{A1.3}$$

where V is the volume of a sphere of radius R_V.

$$\eta(t) = \lim_{\substack{N \to \infty \\ V \to \infty}} \left\{ 4\pi/V \int_0^{R_V} \exp[-tn(R)]R^2 \, dR \right\}^N \qquad A1.4$$

Doing this integral and taking the limits gives the following expression.

$$\eta(t) = \exp\left\{ -4\pi\rho \int_0^\infty R^2 (1-\exp[-tn(R)]) dR \right\} \qquad A1.5$$

Integration in the brackets can be easily performed by using eq.4.3

$$\eta(t) = \exp\left\{ -4\pi^{3/2}\rho \, \frac{d^3}{3} \left(\frac{t}{\jmath_{tr}}\right)^{1/2} \right\} \qquad A1.6$$

Now the concentration of Mn in mole fraction can be represented in terms of ρ and d (next neighbour distance) considering Zn substitutes Zn in the ZnS lattice. There are four atom sites per unit cell and $d=a/\sqrt{2}$, where a is lattice parameter (for zinc blende structure). Final relationship is given below (result will be same for wurtzite structure).

$$C_{\bar{Mn}} = \frac{2^{3/2} \, \rho \, d^3}{4} \qquad A1.7$$

Then,

$$\eta(t) = \exp\left\{ -\mu\pi^{3/2} C_{Mn} \left(\frac{t}{\jmath_{tr}}\right)^{1/2} \right\} \qquad A1.8$$

where μ is approx. unity. This is the expression for $\eta(t)$, the probability that an excited atom is still excited at time t, if it was excited at t=0.

Appendix II

Consider a chain of energy transfer over Mn ions. Probability of energy loss at any ion is P_{cap}. Therefore, the probability that the excitation has not reached a trap after n hops of the energy is $\sim (1-P_{cap})^n$. We now define τ_e to be the effective decay-time for the ensemble loss process, when

$$(1-P_{cap})^n = \frac{1}{e} \qquad\qquad A2.1$$

From the definition of the exponential function, we know that for large value of n [48],

$$P_{cap} = 1/n \qquad\qquad A2.2$$

Now, $\tau_e = n\,\tau_{hop}$

where τ_{hop} is already defined in the text (refer to 4.2) or

$$\tau_e = \frac{\tau_{hop}}{P_{cap}} \qquad\qquad A2.3$$

The only requirement for eq.A2.3 to be true is that P_{cap} should be small or n should be large.