

ANALYSIS OF POLYMORPHIC PROPERTIES OF ZnS(Mn)  
BY LASER SPECTROSCOPY

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Site selected laser spectroscopy has been used for investigating polymorphic properties of ZnS(Mn) by taking advantage of the spectral shift of both luminescence emission and excitation of  $Mn^{2+}$  on different lattice sites. Besides the four main sites five more sites are identified. The inhomogeneous broadening is explained by the difference of radii of  $Zn^{2+}$  and  $Mn^{2+}$ .

### 1. Introduction

Laser spectroscopy is a powerful tool for investigating the interaction of ions within luminescent crystals. This method has already been used for analyzing the interaction of Mn-pairs in ZnS by time resolved spectroscopy [1] and for identifying the luminescence of  $Mn^{2+}$  on three inequivalent lattice sites in polymorphic ZnS [2].

ZnS can be grown with the polytypes corresponding to the sequence ABCA... (zincblende, site symmetry  $T_d$ ), with the sequence ABA... (wurtzite, site symmetry  $C_{3v}$ ) and with varying stacking sequence along the  $[111]_w$  axis. The sequence of stacking faults (SF) can be regular, e.g. with the polytypes 4H, 6H and 9R, or irregular. In both cases we have inequivalent sites with trigonal symmetry  $C_{3v}$ . The number of possible sites depends on the number of double layers, which are included in the consideration.

Mn is an appropriate indicator for studying the polymorphic properties because its luminescence is sensitive to the crystalline environment, but its valence state  $Mn^{2+}$  can not be changed by visible radiation.

A model for the optical vibronic states on  $Mn^{2+}$  in polymorphic ZnS by dynamical Jahn-Teller effect considering the four main sites of polymorphic ZnS is given by Parrot et al. [3].

The main purpose of the present paper is to identify the influence of more distant stacking faults and the combined action of several stacking faults on the luminescent properties of ZnS, which can be predicted by simple symmetry considerations. Moreover we report on the influence of lattice sites on the decay time of luminescence which is related to the oscillator strength of the internal transition  $4T_1 \rightarrow 6A_1$  of  $Mn^{2+}$ . Finally we tried to obtain the parameters which induce the inhomogeneous line broadening of the fundamental vibronic lines (FVL).

## 2. Experimental

The ZnS crystals were activated by different amounts of manganese. They were kept in a cryostat at 4.2 K and excited by a nitrogen pumped dye laser with a pulse peak power of about  $10^5$  W and a pulse time of 10 ns. For registering the luminescence we used a grating spectrometer, a photon counting system and an averaging system.

## 3. Results

In addition to the results we obtained earlier [2] we were able to analyze the  $Mn^{2+}$  on a nearly hexagonal site (PS) which was already mentioned by Lambert et al. [4.5]. We excited within the line  $21332\text{ cm}^{-1}$  ( $6A_1 \rightarrow 4E$ , PS) and observed the corresponding emission line centered at  $18095\text{ cm}^{-1}$  ( $4T_1 \rightarrow 6A_1$ , PS). In the same way we obtained the excitation line due to  $6A_1 \rightarrow 4T_2$  for  $Mn^{2+}$  on a PS site (Fig.1).

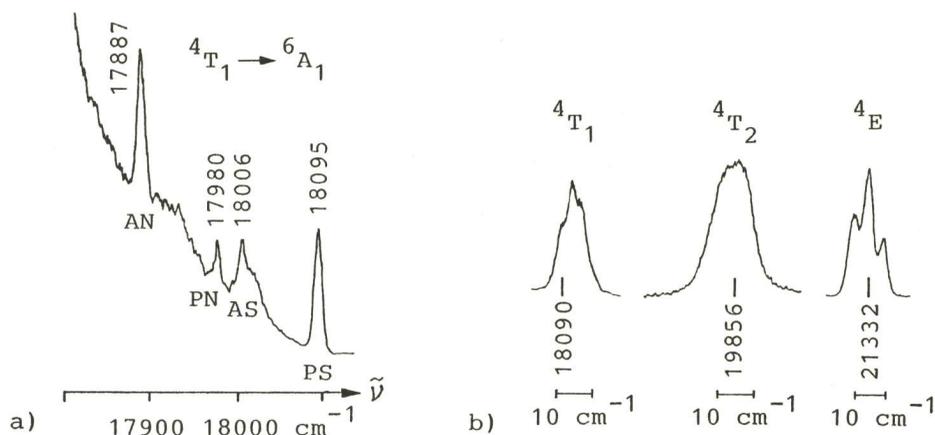


Fig.(1)  $Mn^{2+}$  on a PS site in ZnS ( $10^{-4}Mn$ );  $T = 4.2\text{ K}$   
 a) emission spectrum excited within the line  $\tilde{\nu} = 21332\text{ cm}^{-1}$   
 b) FVLs of emission and excitation

As we expect from earlier measurements there should be more lines hidden in the spectra. We clarified these structures by using a "contour line analysis". We registered only a small part  $\Delta\tilde{\nu}_{em}$  of the emission line when varying the wavenumber  $\tilde{\nu}_{ex}$  of the dye laser beam within the corresponding excitation line. This was done step by step for all  $\Delta\tilde{\nu}_{em}$  in the interesting range. The results are combined to a set of curves  $I_{em} = f(\tilde{\nu}_{ex}, \tilde{\nu}_{em})$  in a three-dimensional relief. An example is given in Fig.(2a). From this relief we took the contour lines (Fig.2b). In that way we registered in addition to the site AN three more sites AN1, AN2 and AN3. Within the main system AN also the thermalized line of emission can be seen.

The results of these measurements are summarized in the table.

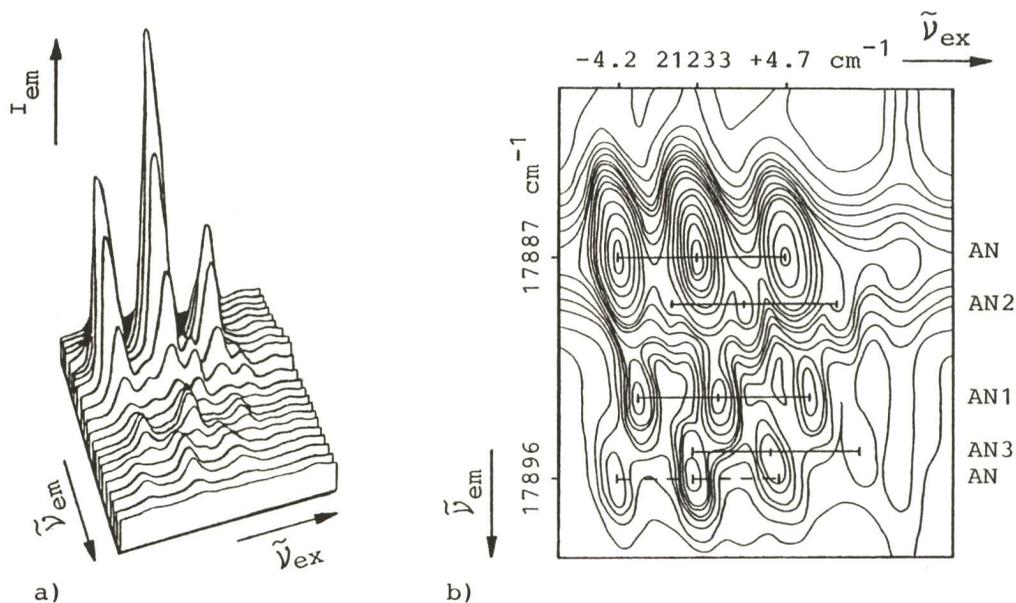


Fig. (2) Combined emission ( ${}^4T_1 \rightarrow {}^6A_1$ ; AN) and excitation ( ${}^6A_1 \rightarrow {}^4E$ ; AN) spectra of ZnS ( $10^{-4}\text{Mn}$ );  $T = 4.2\text{ K}$   
 a) relief b) corresponding contour lines

	$\tilde{\nu}({}^4E) [\text{cm}^{-1}]$				$\tilde{\nu}({}^4T_2) [\text{cm}^{-1}]$				$\tilde{\nu}({}^4T_1) [\text{cm}^{-1}]$			$\tau$ (ms)
	$\Delta\tilde{\nu}$	$\Gamma_8$	$\Gamma_7$	$\Gamma_6$	$\Delta\tilde{\nu}$	$\Gamma_8(\frac{5}{2})$	$\Gamma_6$	$\Gamma_8(\frac{3}{2})$	$\Delta\tilde{\nu}$			
cub												
AN	0	21233	-4.2	+4.7	0	19676	+3.9	+34	0	17887	+9.3	1.77
AN1	+1.2	21234	-4.3	+4.9	-	-	-	-	+5.6	17893	+9.4	
AN2	+2.6	21236	-4.1	+5.0	-	-	-	-	+1.9	17889	+9.5	
AN3	+3.9	21237	-	+4.9	-	-	-	-	+7.8	17895	-	
ax1												
AS	+15.1	21248	-4.3	+4.7	+86.4	19763	0	+42	+118.7	18006	+9.4	1.30
AS2	+17.5	21251	-4.2	+4.7	-	-	-	-	+120.5	18008	+9.5	
ax2												
PN	+85.6	21319	-4.3	+5.1	+97.7	19774	+6.0	+37	+90.4	17977	+2.6/8.8/12.4	1.62
PN1	+87.5	21321	-4.2	+5.1	-	-	-	-	+99.1	17986	+2.1/9.1/13.2	
hex												
PS	+99.3	21332	-4.1	+5.0	+180	19856	-	-	+203	18090	+4/7/13/17/22	1.15

As for the dependence of the decay time  $\tau$  of luminescence on different crystal sites the new results follow the line of measurements reported earlier [2]. The decay time  $\tau$  of the luminescence of  $\text{Mn}^{2+}$  on a PS site is clearly shorter than the corresponding times of  $\text{Mn}^{2+}$  on the other sites. However within the limits of our present measurements, there is only one decaytime for all subsystem of one main system. So far time resolved spectroscopy does not seem to be helpfull for discriminating small differences in environmental distortion.

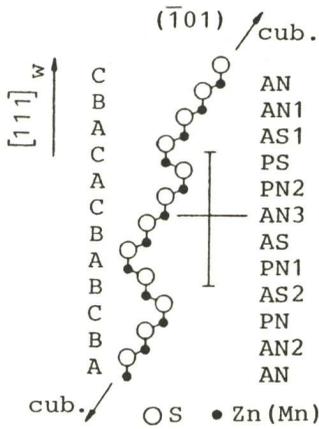


Fig. (3)

Figure (3) illustrates 11 out of 16 possible inequivalent sites, which may appear within a range of 6 double layers of polymorphic ZnS as grown in the direction  $[111]_w$  for the distorted cubic crystals.

The assignments in Fig.(3) are determined in the following way. We started from AN and compared the shift of AS and AN1. The shift of AS and AN1 against AN behaves in the emission band and in the excitation band similarly as shown in the table. From this we conclude that AN1 has a distance of one double layer more than AS from the stacking fault. As further criterion for finding the correct assignment we used the simultaneous appearance of lines: AS, PN, AN1 and AN2 are connected to one SF; AS2 and PN1 to two SFs (corresponding to 4H). We were not yet able to identify AS1 and PN2. Following our considerations they should appear simultaneously with PS (two SF, corresponding to 2H).

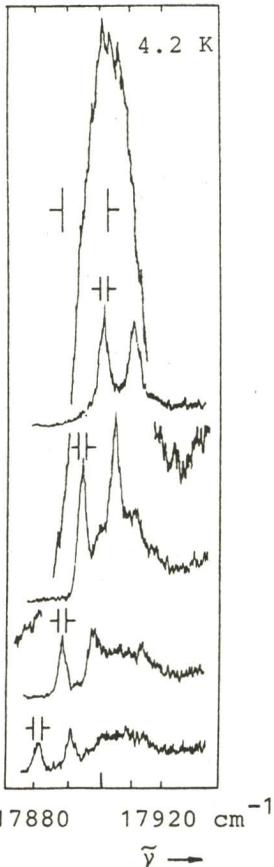


Fig. (4) Excitation spectra  ${}^6A_1 \rightarrow {}^4T_1$  (AN) of ZnS( $10^{-2}\text{Mn}$ )

For all FVLs of the luminescence spectra we observed an inhomogeneous line broadening. This effect, which is already registered at low concentrations of Mn, increases with increasing amount of the activator. Figure (4) gives as an example the excitation spectrum of the transition  ${}^6A_1 \rightarrow {}^4T_1$  of ZnS( $10^{-2}\text{Mn}$ ) at different emission energies  $\bar{\nu}_{em}$  which is indicated above each curve by the width and position of slit. All observed lines are shifted drastically, but no new structure appears. We explain this inhomogeneous line broadening by fluctuations of the lattice constant [6]. The radii of  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$  differ at about 8%. This seems sufficient to introduce internal pressure and change of the crystal field parameter  $Dq$ .

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