

# Energy Transfer Between Fe<sup>2+</sup> Centers in Polymorphic ZnS

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## Abstract

High resolution Fourier transform spectroscopy of the Fe<sup>2+</sup> luminescence and absorption in polymorphic ZnS is performed to study the energy transfer (cross-relaxation) mechanism between different polytypic Fe<sup>2+</sup> centers. To get further insight into these processes calorimetric absorption and transmission spectroscopy have been used to determine quantitatively the non-radiative relaxation of the Fe<sup>2+</sup> transition. We obtain quantum efficiencies, i. e. the radiative recombination part, of 10% and 20% for the <sup>5</sup>T<sub>2</sub> ↔ <sup>5</sup>E transition of the cubic and the two axially distorted Fe<sup>2+</sup> centers, respectively. With increasing Fe concentration this behaviour is changed, the radiative relaxation is now decreased for the Fe<sup>2+</sup> centers with higher transition energy.

## I. Introduction

ZnS is a promising material for visible and ultraviolet photonic devices. The luminescence efficiency of these devices strongly depends on the impurity content. Therefore, there is considerable interest in the influence of substitutionally incorporated transition metals on the optical properties of ZnS. Especially, iron is a prominent killer of visible luminescence bands in ZnS and gives rise to intense infrared Fe<sup>2+</sup> [1] and Fe<sup>3+</sup> [2] emission bands.

Recently, Fuchs and Koidl [3] gave evidence for an energy transfer mechanism (cross relaxation) between different Co<sup>2+</sup> centers in structurally pure 4H ZnS using Fourier-transform photoluminescence excitation spectroscopy. They demonstrated that about 75% of the photoexcited quasi hexagonal Co<sup>2+</sup> centers transferred their excitation energy to the quasi cubic centers leading to strong enhancement of the luminescence of this center.

The purpose of this paper is to clarify the influence of the polymorphic crystal structure on the <sup>5</sup>T<sub>2</sub> ↔ <sup>5</sup>E transition of Fe<sup>2+</sup> and to investigate the nonradiative relaxation processes of iron which is known to exhibit much faster relaxation rates (5.5 μs [4]) compared to the Co<sup>2+</sup> center (some ms [5]). High resolution Fourier-spectroscopy of ZnS crystals with different polytypic parts has led to the detection of various Fe<sup>2+</sup> zero phonon lines (ZPLs) in absorption and emission. The intensities of these ZPLs in different samples are compared. Furthermore, calorimetric absorption and transmission spectroscopy (CAS/CTS) has been performed to get knowledge about the quantum efficiencies of the internal Fe<sup>2+</sup> transitions yielding new arguments for energy transfer processes between different Fe<sup>2+</sup> centers in ZnS.

## II. Experimental technique

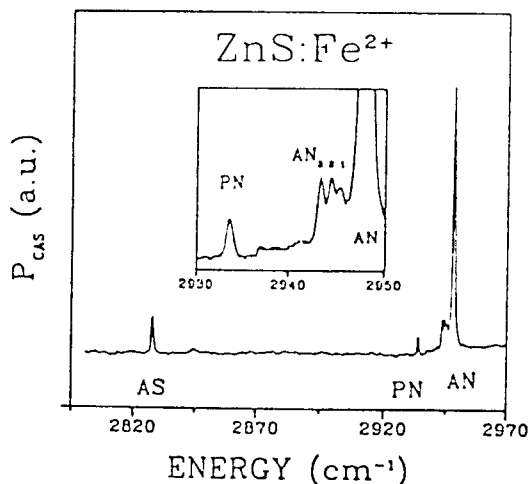
The photoluminescence and absorbance experiments were performed with a Fourier-transform spectrometer (BONEM DA.3) using a InSb diode operating at 77K for detection [3]. As excitation source for the luminescence experiments served the 476 nm line of an Ar ion laser. The calorimetric absorption and transmission experiments are performed using a <sup>3</sup>He/<sup>4</sup>He-dilution refrigerator. The CAS spectra are taken by measuring the sample temperature in dependence of the excitation wavelength, while in the CTS spectra the transmitted light power is calorimetrically detected. Both CAS and CTS give quantitative results allowing the determination of quantum efficiencies. The experimental setup is described in detail in ref. [6].

The investigated ZnS crystals were grown by the Frerich-Warminsky method [7] and were doped during the growing procedure.

### III. Experimental Results

All modifications of ZnS consist of sequences of Zn-S layers being stacked along the  $(111)_g$  direction of growth. Transition metal impurities substituting  $Zn^{2+}$  ions are located in a tetrahedrally coordinated  $S^{2-}$  environment which belongs to two Zn-S layers. The arrangement of the next nearest neighbours from  $Zn^{2+}$  lattice sites differs according to their relative position to stacking faults. Four different lattices sites exist for a substitutional Fe center in dependence on the arrangement of the three nearest neighbors. The four sites are called AN (cubic), AS, PN (axially distorted), and PS (hexagonal) [8]. P indicates a prismatic, A an antiprismatic coordination, S the existence of a single third neighbour on the stacking axis, N its absence. In Fig. 1 a typical calorimetric absorption (CAS) spectrum of  ${}^5T_2 \leftrightarrow {}^5E$  transition of  $Fe^{2+}$  in polymorphic ZnS is shown. Since these investigations are performed at 45 mK, only the fine structure of the  ${}^5T_2$  state of the  $Fe^{2+}$  can be detected. Due to the highly sensitive detecting system of CAS we are able to resolve in addition to the zero-phonon lines (ZPL) of the AN, PN and AS center a series of new ZPLs which can be interpreted as subcenters  $AN_{1,2,3}$  of the cubic center (see the insert of Fig. 1). This attribution is in excellent agreement with the  $Fe^{3+}$  center in polymorphic ZnS [2] and also with the observed intensity of the polytypic  $Cu^{2+}$  centers in these crystals [9].

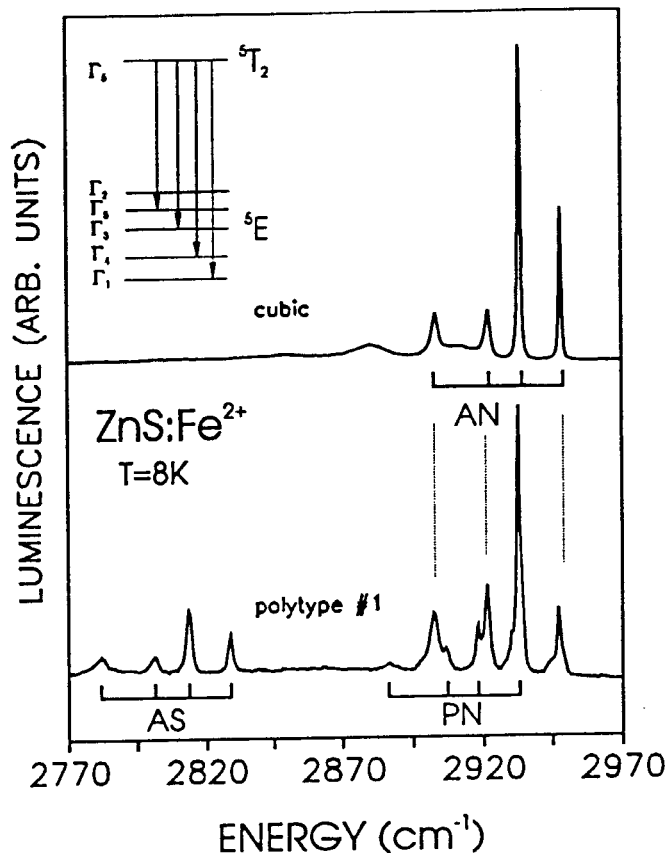
*Fig. 1:*  
High-resolution CAS spectrum of the  ${}^5E \rightarrow {}^5T_2$   $Fe^{2+}$  transition in polymorphic ZnS at  $T=45mK$ . Additionally to the main polytypic centers the subcenters of AN are also observed (see insert).



In a dominantly cubic ZnS crystal with microtwins (or stacking faults) each twin boundary induced the same number of AS and PN sites. In fact, the integrated absorbance of the ZPLs of the AS and PN centers is equal within 1%, indicating a statistical incorporation of  $Fe^{2+}$ . The  $Fe^{2+}$  transition of the AS center is very similar to that of the PN one, but is shifted by 104.3  $cm^{-1}$  towards lower energies. In Fig. 2 the luminescence spectra of the  ${}^5T_2 \leftrightarrow {}^5E$  transition of  $Fe^{2+}$  in completely cubic (a) and mixed polytypic (b) ZnS at 8 K are seen. In the well-known cubic spectrum the allowed transitions from the  $\Gamma_5$  level of the  ${}^5T_2$  state to the spin-orbit components of the  ${}^5E$  state are clearly resolved (see level scheme in the insert). The polymorphic crystal exhibits a superposition of the spectra (lower spectrum) of the cubic and different axial centers. The energy shifts  $\Delta E(AN)$  of the different AS, PN and PS  $Fe^{2+}$  defect centers compared to the AN ZPL (Tab. 1) leads to the conclusion that the empirically known superposition principle [8], which describes the influence of stacking faults on the transition metal energy level as a superposition of the crystal fields induced by each stacking layer, is also valid for  $Fe^{2+}$  centers. With the formula  $E(AN) + \Delta E(AS) + \Delta E(PN) = E(PS)$  the energy of the

center of gravity of the  $\Gamma_5(^5T_2) \leftrightarrow \Gamma_1(^5E)$  transition of the PS center can be determined at  $2821.4 \text{ cm}^{-1}$ , which is in good agreement with ref. [10]. In Tab. 1 the observed zero-phonon energies of the different polytypic centers of the  $^5T_2 \leftrightarrow ^5E$  transitions in ZnS and the energy splitting of the  $\text{Fe}^{2+}$  levels are summarized.

**Fig. 2:**  
Luminescence spectra of a cubic (upper curve) and a polymorphic (lower curve) ZnS crystal.

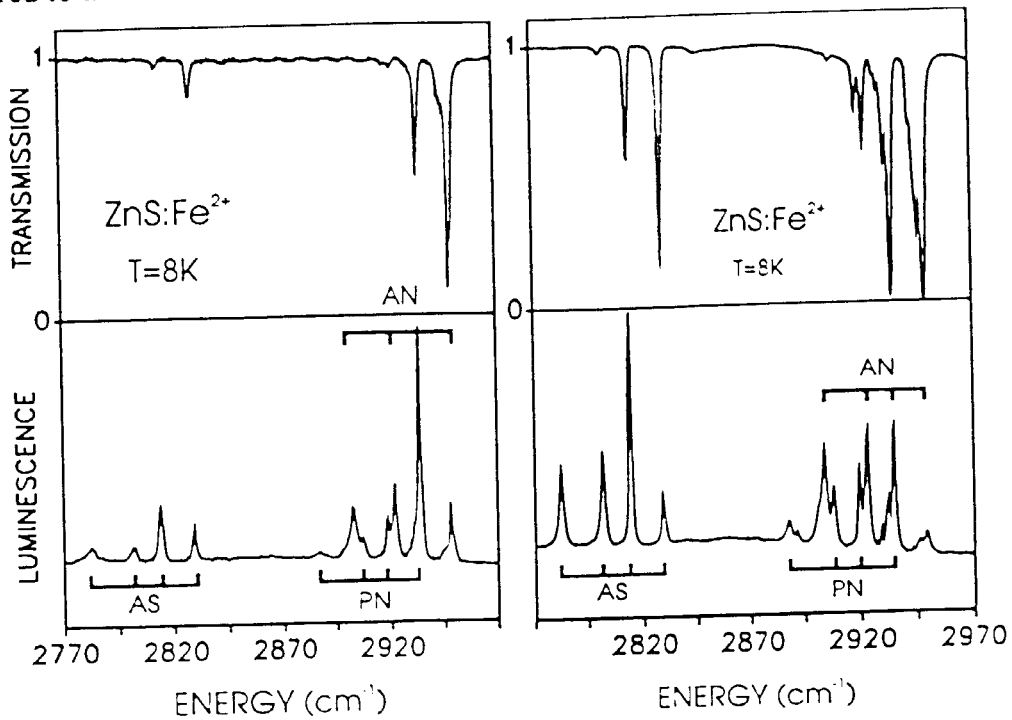


CENTER		$\Gamma_1$	$\Gamma_4$	$\Gamma_3$	$\Gamma_5$	$\Gamma_2$	$\Delta E(\text{AN})$
AN	E ( $\text{cm}^{-1}$ )	2947.9	2933.1	2922.0	2902.5		0
	$\Delta(^5E)$	0	14.8	25.9	45.4		
AN <sub>1</sub>	E ( $\text{cm}^{-1}$ )	2945.5	2930.7				2.4
	$\Delta(^5E)$	0	14.8				
AN <sub>2</sub>	E ( $\text{cm}^{-1}$ )	2944.7	2929.9				3.2
	$\Delta(^5E)$	0	14.8				
AN <sub>3</sub>	E ( $\text{cm}^{-1}$ )	2943.7	2928.9				4.2
	$\Delta(^5E)$	0	14.8				
PN	E ( $\text{cm}^{-1}$ )	2933.7	2918.4	2907.0	2889.7	2886.7	14.2
	$\Delta(^5E)$	0	15.3	26.7	44.0	47.0	
AS	E ( $\text{cm}^{-1}$ )	2829.4	2813.9	2801.3	2772.5		118.5
	$\Delta(^5E)$	0	15.5	28.1	56.9		

**Tab. 1:** Energies of the ZPLs of the different  $\text{Fe}^{2+}$  centers in polymorphic ZnS. The splitting  $\Delta$  of the  $^5E$  ground state is given, and the shift  $\Delta E(\text{AN})$  of the different  $\Gamma_5(^5T_2) \leftrightarrow \Gamma_1(^5E)$   $\text{Fe}^{2+}$  ZPLs with respect to the cubic transition is also indicated.

In Fig. 3 transmission and luminescence spectra of a highly iron doped polymorphic ZnS crystal (right picture) are compared to that of a low doped ZnS (left picture). As a striking fact we found that the *relative* luminescence intensities of different polytypic centers differ strongly with increasing Fe concentrations. From the different strength of the AS- and PN- related absorption lines a predominant PN-type  $\text{Fe}^{2+}$  surrounding can be followed, but, in

contradiction, the intensity of the AS center related emission is enhanced by a factor of 3 compared to that of the PN center.



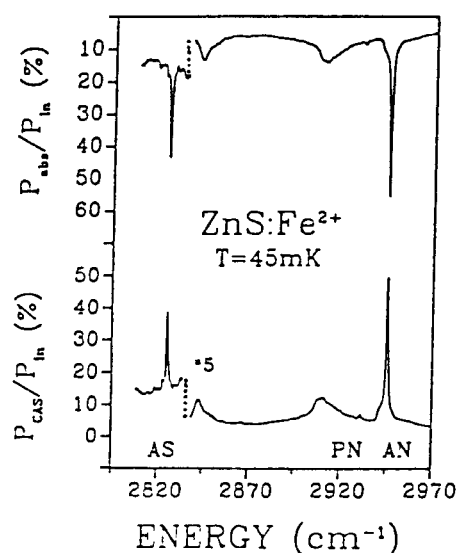
*Fig. 3:* Transmission and luminescence spectra of a highly iron doped polymorphic ZnS crystal (right picture) are compared to that of a low doped ZnS (left picture).

To clarify the mechanism leading to the strong enhancement of the PL of the center with lower transition energy we performed calorimetric absorption (CAS) and transmission (CTS) spectroscopy at mK temperatures. Typical spectra are shown in Fig. 4. Since only the lowest fine structure component of the  ${}^5E$  ground state is populated at 45 mK, in Fig. 4 no "hot lines" are observed (as it was the case in Fig. 3). Furthermore, the quantum efficiency of the  ${}^5T_2$  level can be determined by comparing  $P_{\text{abs}}$ , the light power absorbed by the sample, and  $P_{\text{CAS}}$ , that part of  $P_{\text{abs}}$  which is converted into heat. We calculated a quantum efficiency of 10% for the cubic center, whereas the quantum efficiency of the axial centers amounts to 20% in the low iron doped ZnS crystal.

#### IV. Discussion

The most interesting aspect in section III is the strong enhancement of the luminescence intensity of the low energy AS center in highly iron doped ZnS crystals, whereas the intensities of other  $\text{Fe}^{2+}$  centers decrease. Three kinds of different mechanisms could be responsible for that behaviour: self-absorption processes, different ratios of the radiative/non-radiative processes (especially for the AN, PN and AS centers) or an energy transfer process between the axially distorted  $\text{Fe}^{2+}$  centers.

The self-absorption process as possible explanation can be excluded since the self-absorption influences predominantly the emission line, which recombines in the ground state, and not luminescence lines, which decay radiatively to the excited  ${}^5E$  states with no corresponding low temperature absorption lines.



**Fig. 4:**  
Calorimetric absorption and transmission spectra of a weakly Fe-doped polymorphic ZnS crystal at 45mK.

The quantum efficiencies of the axially distorted ZPLs in low doped crystals are always 20%, i. e. the radiative decay rate for all axial  $\text{Fe}^{2+}$  centers is the same. Thus, we observe a strong non-radiative part of 80% for the recombination from the excited  $T_2$  level into the  $^5E$   $\text{Fe}^{2+}$  ground state. This shows unambiguously that the enhancement of the AS center compared PN center cannot be explained by a change of the non-radiative processes.

We propose therefore that the enhancement of the AS luminescence in highly Fe doped ZnS crystals is caused by a phonon assisted energy transfer processes from the high energy to the low energy  $\text{Fe}^{2+}$  centers. In analogy to the observations in different Co centers in structural pure 4H ZnS [6], this behaviour can be understood in the following way: After photoexcitation of the  $\text{Fe}^{2+}$  center the ion relaxes into the  $^5T_2$  state, the initial state under discussion. Within the lifetime of the  $^5T_2$  state there is a high probability of an energy transfer process to an ion in the spatial environment. The transfer process from the cubic system to the PN or to AS center with at least  $118 \text{ cm}^{-1}$  lower excitation energies is strongly favoured against the inverse process. The excess energy is well within the one phonon density of states of ZnS. The probability of such a transfer process depends on the Fe concentration and on the life time of the excited state. The lifetime of the  $^5T_2$  state of  $\text{Fe}^{2+}$  in ZnS amounts to  $5.5 \mu\text{s}$  [4]. This explains why the efficiency of the  $\text{Fe}^{2+}$  cross-relaxation is smaller than that of the  $\text{Co}^{2+}$ . Thus, it could be demonstrated that even in the case of low transition lifetimes of only some  $\mu\text{s}$  cross relaxation is a prominent de-excitation channel of transition metal impurities.

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