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# Nonradiative transition rates of $\text{Fe}^{2+}$ in III–V and II–VI semiconductors

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## Abstract

Calorimetric absorption and transmission spectroscopy at mK temperatures has been performed to determine the quantum efficiency of the internal  $\text{Fe}^{2+}$  ( ${}^5\text{T}_2 \rightarrow {}^5\text{E}$ ) transition in different semiconductors. Experimental results are presented for III–V (GaAs, GaP, InP) and II–VI (ZnS, ZnO, CdS) semiconductors. The transition rates of the competing radiative and nonradiative processes in different host lattices are discussed.

## 1. Introduction

Iron is a prominent dopant in both III–V and II–VI compounds and is thus very suitable as a model system to study the influence of the host crystal to an impurity ion. Iron has been extensively investigated [1–5] and, as a result, today the energy level scheme is well established [6]. Nevertheless, to date there is only little knowledge about the dynamical behaviour of  $\text{Fe}^{2+}$  and especially the nonradiative relaxation of the impurity has not yet been studied systematically.

Since internal 3d transitions are dipole-forbidden by Laporte's rule nonradiative decay is assumed to play a predominant role for the relaxation process. However, often intense Fe-correlated luminescence bands have been observed [1–6] proving a nonvanishing probability for radiative decay. In this paper we report on the quantum efficiency of the  ${}^5\text{T}_2 \rightarrow {}^5\text{E}$  transition of  $\text{Fe}^{2+}$  in different host crystals to serve as a model system for studying the

influence of the vicinity of the impurity ion to its internal relaxation process.

## 2. Experimental technique

Calorimetric absorption spectroscopy (CAS) at mK temperatures [7] detects the increase of sample temperature caused by the generation of phonons during the relaxation of (photo-)excited carriers to thermal equilibrium. By this technique the nonradiative relaxation is measured quantitatively, and since the absorbed light power  $P_{\text{abs}}$  can be derived from the calorimetric measurement of the transmission (CTS) the total nonradiative recombination part  $q = P_{\text{CAS}}/P_{\text{abs}}$  can be determined from a simultaneous CAS/CTS experiment. Thus CAS at mK temperatures has become a very powerful tool to determine the quantum efficiency  $\eta$  of excited states in solids.

As the relaxation within the  ${}^5\text{T}_2$  excited state is fast and the fine structure splitting of the  ${}^5\text{E}$  ground state is small [1–6] the system can be treated in

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terms of a two-level system. In this case the transition probability  $W$  from the excited state to the ground state consists of two parts  $W_r$  and  $W_{nr}$  for the radiative and the nonradiative transition rate, respectively:  $W = W_r + W_{nr}$ . Since the transition probability  $W$  can be evaluated from the luminescence decay time  $\tau$  ( $W = 1/\tau$ ) and the radiative decay part

$$\eta = 1 - q = 1 - (P_{CAS}/P_{abs}) \quad (1)$$

results from the CAS/CTS experiment, we are able to determine the radiative and nonradiative transition rates:

$$W_{nr} = (1 - \eta)W = \frac{1 - \eta}{\tau}, \quad (2)$$

$$W_r = \eta W = \frac{\eta}{\tau}. \quad (3)$$

### 3. Experimental results

At mK temperatures there is no thermal excitation within the  $^5E$  ground state. Selection rules allow optical transitions from the  $\Gamma_1$  ground state only to  $\Gamma_5$  levels of the excited  $^5T_2$  state in  $T_d$  symmetry (see Fig. 1). Hexagonal ( $c_{3v}$ ) crystals exhibit an additional splitting of fine structure levels, and observed transitions are also indicated.

#### 3.1. III-V compounds

Experimental results of Fe-doped III-V semiconductors GaAs, GaP and InP with cubic crystal symmetry are shown in Fig. 2. The CAS spectra are compared to the absorbed light power which was evaluated from the transmission spectra.

In all crystals two zero-phonon absorption lines can be observed, attributed to the  $Fe^{2+}$  ( $^5E \rightarrow ^5T_2$ ) transitions (labeled  $\Gamma_5$  and  $\Gamma'_5$ ) [3–5]. However, spectra of both phosphorus-compounds differ significantly from the GaAs spectrum. While in InP and GaP the  $\Gamma'_5$  absorption can be clearly detected as a broad line, in GaAs this resonance is very small. Furthermore, in InP and GaP the coupling to a defect-related phonon appears as a sharp peak labeled GM (gap mode) whereas no

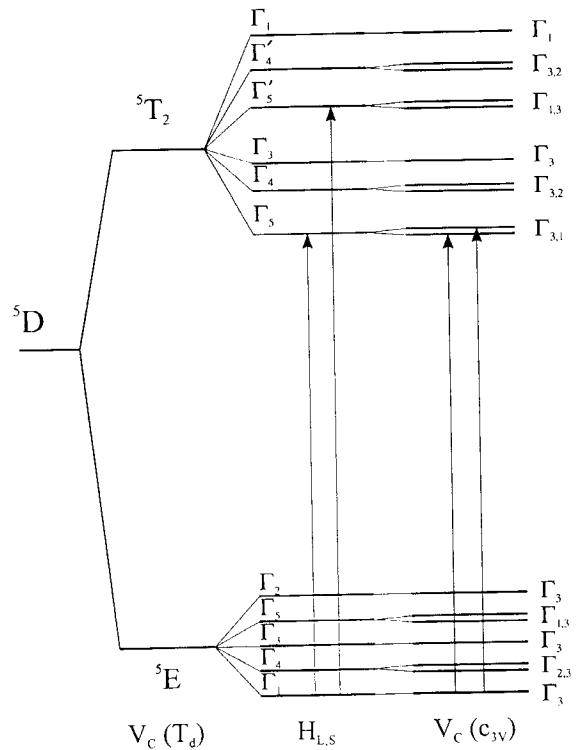


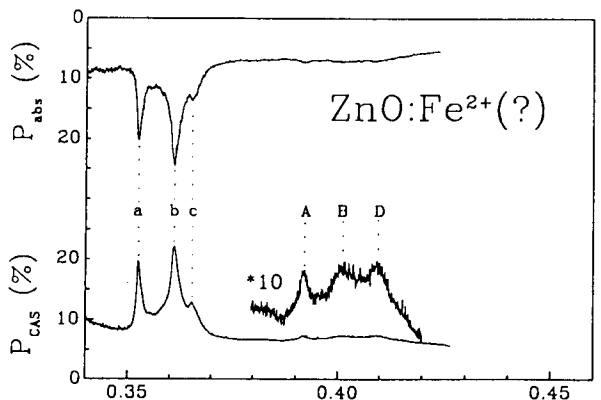
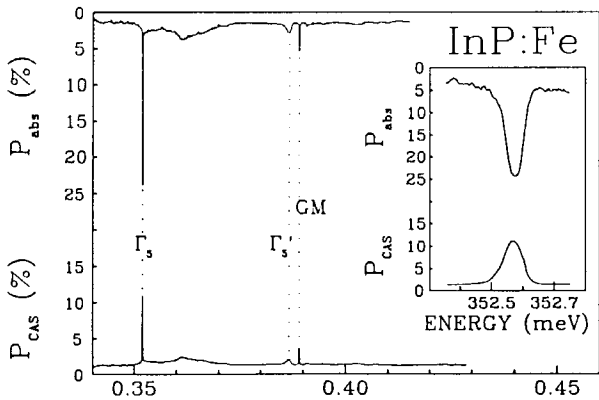
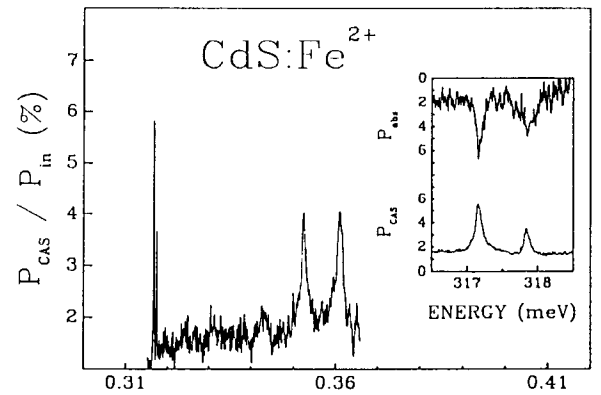
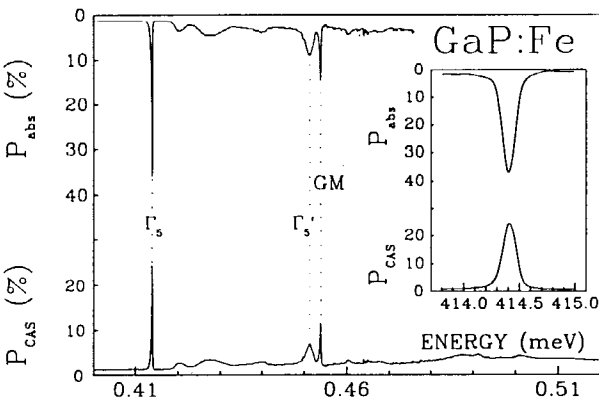
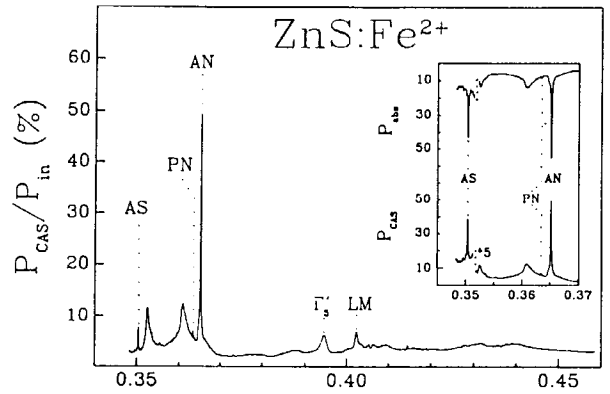
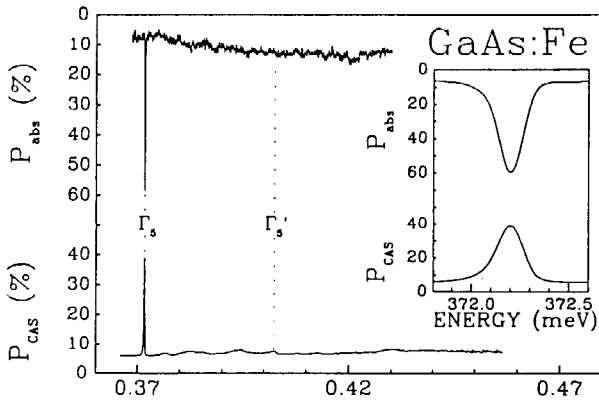
Fig. 1. Level scheme of  $Fe^{2+}$  under the influence of the crystal field and spin-orbit interaction. Observed absorptions are indicated by an arrow.

significant phonon mode can be observed in GaAs.

The quantum efficiency  $\eta$  of the internal  $Fe^{2+}$  transition is determined from the  $P_{CAS}$  and  $P_{abs}$  spectra of Fig. 2 by comparing the magnitude of the absorption peaks according to Eq. (1). Values of  $\eta$  of  $26\% \pm 4\%$ ,  $47\% \pm 6\%$  and  $35\% \pm 5\%$  for the  $Fe^{2+}$  ( $^5T_2 \rightarrow ^5E$ ) transition in GaP, InP and GaAs result, respectively.

#### 3.2. II-VI compounds

A typical absorption spectrum of polymorphic  $ZnS:Fe^{2+}$  is shown in the upper part of Fig. 3. It resembles very much those of the III-V compounds because our sample is mostly cubic. However, on the low-energy side of the intense cubic (AN) line some more lines appear due to the polymorphic crystal structure of ZnS. We obtain values of the



ENERGY (eV)

ENERGY (eV)

Fig. 2. Calorimetric absorption spectra in comparison to the absorbed light power of the  $Fe^{2+}$  ( ${}^5E \rightarrow {}^5T_2$ ) transition in InP, GaP and GaAs. In the inset detailed spectra of the  $\Gamma_5$  zero phonon lines are shown.

Fig. 3. Calorimetric absorption spectra in comparison to the absorbed light power of the  $Fe^{2+}$  ( ${}^5E \rightarrow {}^5T_2$ ) transition in ZnS, CdS, ZnO.

quantum efficiency  $\eta$  of 20% for AS and PN, but only 10% for the high energy AN line.

In CdS the host lattice exhibits only a hexagonal structure. The  $\text{Fe}^{2+}({}^5\text{T}_2)$  levels therefore reveal a further splitting due to the trigonal field. A typical spectrum of a weakly Fe-doped CdS sample is shown in the middle part of Fig. 3. A sharp doublet around 0.32 eV appears due to the transition from the  ${}^5\text{E}(\Gamma_1)$  ground state to the two  ${}^5\text{T}_2(\Gamma_5)$  sub-levels. Furthermore, two broad absorptions can be observed 44 and 55 meV on the high-energy side of the zero-phonon doublet. The nature of these features whether phonon replicas or no-phonon lines of higher excited states is not yet clear. The quantum efficiency of the zero-phonon doublet around 0.32 eV amounts to  $12\% \pm 4\%$ .

Experiments on  $\text{Fe}^{2+}$  in ZnO have not been reported as yet. The absorptions showing our ZnO sample (Fig. 3, lower curve) cannot be attributed to any impurity known in ZnO to date. Their quantum efficiency is close to zero within the experimental error, and for the following reasons we attribute them to  $\text{Fe}^{2+}$  in ZnO:

- 1) From the observation of an  $\text{Fe}^{3+}$  related luminescence we know that our sample contains iron [8].
- 2) The energy range of the observed structure is typical for  $\text{Fe}^{2+}$  transitions.
- 3) The weak structures A, B observed between 0.39 and 0.41 eV are both 39 meV above the similar looking, intense lines a, b. This energy difference does not correspond to a host phonon mode but, however, it is in the energy range of Fe-related local vibrational modes observed in other semiconductors [1,3–5].

#### 4. Discussion

Our experimental results are summarized in Table 1. Here, the nonradiative and radiative transition rates ( $W_{\text{nr}}$  and  $W_{\text{r}}$ ) are also listed. They have been evaluated from the luminescence decay times  $\tau$  taken from literature and the quantum efficiencies  $\eta$  according to Eqs. (2) and (3).

It is a striking fact that the radiative transition rates of the  ${}^5\text{T}_2 \rightarrow {}^5\text{E}$   $\text{Fe}^{2+}$  relaxation are in the same range in all III–V compounds. The shorter

Table 1

Values of the quantum efficiency, luminescence decay time and the radiative and nonradiative transition rates of the  $\text{Fe}^{2+}({}^5\text{T}_2 \rightarrow {}^5\text{E})$  transition in III–V and II–VI semiconductors

	$\eta$ [%]	$\tau$ [ $\mu\text{s}$ ]	$W_{\text{r}}$ [ $\text{s}^{-1}$ ]	$W_{\text{nr}}$ [ $\text{s}^{-1}$ ]
GaAs	35	8.5 [3]	$4.1 \times 10^4$	$7.7 \times 10^4$
GaP	26	6.6 [9]	$3.9 \times 10^4$	$11.4 \times 10^4$
InP	47	11 [10]	$4.3 \times 10^4$	$5.7 \times 10^4$
ZnO	0	–	–	–
CdS	12	–	–	–
ZnS (AN)	10	5.5 [11]	$1.8 \times 10^4$	$16.5 \times 10^4$
ZnS (PN, AS)	20	–	–	–

lifetime of the  ${}^5\text{T}_2$  level in GaAs and GaP compared to InP is only due to an enhanced non-radiative transition rate. Our result of equal radiative transition rates in all three III–V semiconductors is in accordance with considerations of Klein et al. [12] and the value of about  $4 \times 10^4$  agrees reasonably with optical absorption experiments where for the dipole transition rate a value of  $6.7 \times 10^4$  has been determined [12].

The internal  $\text{Fe}^{2+}$  relaxation mechanisms in III–V compounds have been discussed already in the past [12]. Three different kinds leading to nonradiative decay have been proposed: 1) Auger processes with shallow bound states close to the conduction band; 2) free carrier capture; and 3) multiphonon emission processes (MPEP). The first two mechanisms can be neglected here since they do not occur in semi-insulating material at low temperatures at sub-charge-transfer excitation. Also nonradiative relaxation via phonon cascade processes can be excluded and therefore we propose a MPEP to be responsible for the non-radiative relaxation. But there are no obvious correlations between the different properties (e.g., the binding properties and the phonon energies) of the III–V compounds and the nonradiative transition rates of  $\text{Fe}^{2+}$  and, thus, no simple model to explain the different nonradiative transition rates in the three materials can be given.

For II–VI compounds there is only little information about the internal  $\text{Fe}^{2+}$  relaxation, and the luminescence decay time has been measured only in cubic ZnS [11]. For polymorphic ZnS

a phonon assisted energy transfer from the high energy cubic AN center to the low-energy PS, AS and PN centers has been established which leads to a decreasing AN luminescence intensity with increasing Fe concentration [14]. But any influence of this energy transfer on the quantum efficiencies of the different centers can be excluded in our weakly Fe-doped crystal. The transition rate of the AN center amounts to  $1.8 \times 10^4 \text{ s}^{-1}$  and is similar to the values of  $\text{Fe}^{2+}$  in III–V compounds. The transition rates of the non-cubic Fe-centers cannot be given due to the lack of time-resolved data but their larger quantum efficiencies suggest an influence by the trigonal crystal field in non-cubic centers.

In CdS also the  $\text{Fe}^{2+} \ ^5\text{T}_2 \rightarrow \ ^5\text{E}$  luminescence has been observed [13]. The lack of time-resolved data does not allow to determine the radiative and non-radiative transition rates at this point. However, the observed quantum efficiency of about 12% indicates similar results to those observed in ZnS.

A very different result has been found for ZnO where a quantum efficiency of zero has been determined for the  $\text{Fe}^{2+}$ -related lines. This experimental fact is in accordance with results obtained for  $\text{Ni}^{2+}$  in ZnO, where also a zero quantum efficiency has been found [15]. Additionally, no  $\text{Fe}^{2+}$  or  $\text{Ni}^{2+}$  luminescence is observed in our samples. The lower quantum efficiencies of  $\text{Ni}^{2+}$  and  $\text{Fe}^{2+}$  compared to CdS and ZnS can be understood as a result of the larger phonon energies in ZnO ( $E_{\text{Phonon}} = 73 \text{ meV}$  (ZnO),  $43 \text{ meV}$  (ZnS),  $38 \text{ meV}$  (CdS)) making a nonradiative MPEP more probable. However, strong  $\text{Fe}^{3+}$  [8] and  $\text{Ni}^{3+}$  [16] luminescence bands are observed in ZnO indicating donor type charge transfer transitions and radiative relaxation only within the  $3+$  charge state. Due to the larger transition energies, the MPEP is quenched here. Similar results have been reported for iron in GaN [17] ( $E_{\text{Phonon}} = 92 \text{ meV}$ ) where also a  $\text{Fe}^{3+}$  but no  $\text{Fe}^{2+}$  luminescence have been observed showing additionally the correlation between phonon energy and nonradiative transition rate.

## 5. Conclusion

In this contribution we presented the quantum efficiencies of the  $\text{Fe}^{2+} (\ ^5\text{E} \leftrightarrow \ ^5\text{T}_2)$  transition in vari-

ous III–V and II–VI semiconductors. It is pointed out that the MPEP is the dominant relaxation channel. The order of magnitude of the MPEP is influenced by the phonon energies as well as of the binding properties of the host compound.

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