

# Fine structure of the $(\text{Fe}^{2+}, \text{h})$ bound states in GaP and InP

L. Podlowski, R. Heitz, T. Wolf, A. Hoffmann, D. Bimberg, and I. Broser

Institut für Festkörperphysik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany

W. Ulrici

Paul-Drude-Institut, Hausvogteiplatz 5-7, 10117 Berlin, Germany

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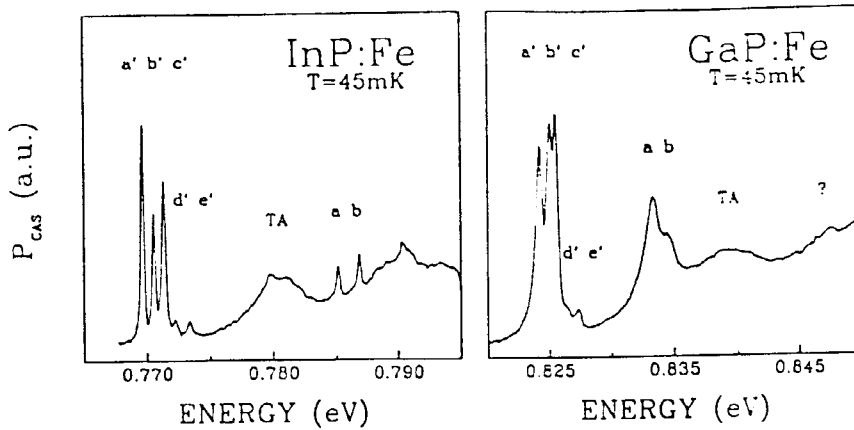
## Abstract

Sharp lines at the onset of the  $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$  charge-transfer band in Fe-doped GaP and InP are attributed to the formation of  $(\text{Fe}^{2+}, \text{h})$  bound states. These lines reveal a strong temperature dependence at mK temperatures due to thermalization effects in the  $\text{Fe}^{3+}$  ( ${}^6\text{A}_1$ ) ground state. A detailed investigation of the temperature dependence of the recently discovered quintett ( $\text{a}' - \text{e}'$ ) and the doublet (a, b) in InP and GaP yields new information concerning the fine structure of the bound  $(\text{Fe}^{2+}, \text{h})$  complex. There is strong evidence that all absorption lines are caused by non-phonon transitions and both series are correlated with different electronic states of the hole. A consistent model for the description of the observed fine structure is presented taking into account the exchange interaction between the localized hole and the impurity centre.

## I. Introduction

Transition metals in III-V semiconductors are of great interest for opto-electronic device applications since some of them have mid-gap energy levels leading to semi-insulating material. Especially, iron in InP has been extensively investigated as a model system to get a detailed understanding of the influence of 3d-impurities on the optical and electrical properties of III-V compounds. In addition to intracentre transitions often broad absorption bands can be observed in Fe-doped material which have been associated to Fe-correlated charge-transfer processes. The  $\text{Fe}^{3+/2+}$  acceptor level is located 0.78eV and 0.84eV above the valence band in InP and GaP, respectively /1, 2, 3/. At the onset of the  $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$  photoionization bands a series of weak narrow lines first have been observed in semi-insulating InP:Fe /3/ triggering a lot of further investigations in various materials. The interpretation of the sharp lines being due to the formation of shallow bound states where the hole is bound to the negatively charged  $\text{Fe}^{2+}$  is now generally accepted, since the appearance of exactly five lines reflects directly the five sublevels of the  $\text{Fe}^{2+}({}^5\text{E})$  term. But there is still a large controversy concerning fine structure details.

In both materials the most significant absorption structure is a quintett labeled ( $\text{a}' - \text{e}'$ ) which occurs around 771meV and 825meV in InP and GaP, respectively (see Fig. 1). On the high energy side the broad band TA is attributed to an acoustical phonon sidewing of the five-fold structure ( $\text{a}' - \text{e}'$ ). Furthermore, in both systems there is one more clearly detectable absorption structure: a doublet labeled (a, b) in both InP and GaP although its appearance is quite different in both materials. The five-fold structure ( $\text{a}' - \text{e}'$ ) appears to be due to the formation of a  $(\text{Fe}^{2+}, \text{h})$  complex, where the hole is in its ground state /1, 4/ but the interpretation of the doublet (a, b) is not as clear. For InP it has been proposed to attribute these lines to the formation of a  $(\text{Fe}^{2+}, \text{h})$  complex too, but with the hole in its first excited state /1, 2/. For GaP the situation is more complicated. There exists two different



**Fig. 1:** High-resolution CAS spectra at the onset of the  $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$  photoionization band in InP and GaP.  $P_{\text{CAS}}$  means heat power produced in the sample and is therefore analogue to an optical absorption scale.

interpretations of (a, b). While some authors describe them in a similar way to in InP /4/, others assign them to be another phonon wing of  $(a' - e')$  /5/ because of their large linewidth. Additionally in GaP some very weak absorptions (?) can be observed which in Ref.5 have been attributed to the first excited state of the hole. Presently no unambiguous experimental results exist to distinguish between no-phonon and phonon associated lines to clarify the observed fine structure.

In this paper results of calorimetric absorption measurements at mK temperatures of Fe-doped InP and GaP are presented. Thermalization effects at these very low temperatures will be demonstrated to yield new information on the electronic fine structure of the  $(\text{Fe}^{2+}, h)$  bound states.

## II. Experimental technique

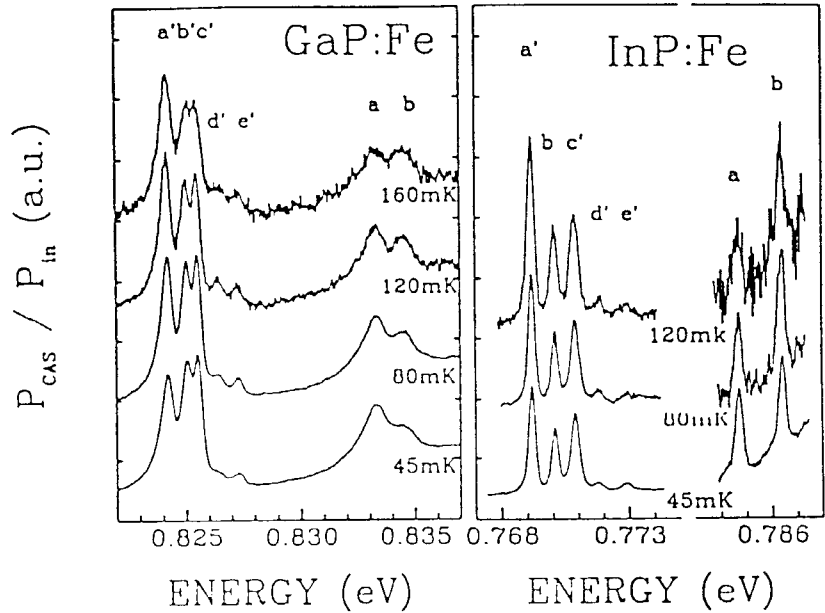
The  $(\text{Fe}^{2+}, h)$  associated absorption lines are very weak calling for a highly sensitive technique to study experimental details. We performed calorimetric absorption spectroscopy (CAS), known to be a powerful tool for the detection of weak signals /6/. Using a  $^3\text{He}/^4\text{He}$ -dilution refrigerator temperature dependent CAS measurements in the mK-region can be performed /7/. The CAS method is based on the detection of the increase of the sample temperature caused by the generation of phonons during the nonradiative relaxation of an excited system to thermal equilibrium. The sample is monochromatically illuminated, and a CAS spectrum is detected by measuring the change of the sample temperature in dependence on excitation wavelength.

## III. Experimental results

High-resolution calorimetric absorption spectra of iron-doped GaP and InP at 45mK are shown in Fig. 1. No thermalization effects of the lines  $(a' - e')$  and (a, b) are observed between 0.5K and 10K indicating that the splittings within the quintett  $(a' - e')$  as well as that of the doublet (a, b) reflects the fine structure of the final state of the transitions.

A significant change of the absorption spectra is observed if the temperature is further decreased to the mK range. The evolution of the spectra between 45mK and 160 mK is shown in Fig. 2. For GaP within the five-fold structure  $(a' - e')$  at 45mK the peak labeled  $c'$  is the most intense one, and  $a'$  is even weaker than  $b'$ . The line  $d'$  is strongly diminished and constitutes as a small shoulder between  $c'$  and  $e'$ . Within the doublet (a, b) the line a is about three times larger, i. e. an inverted intensity ratio compared to "high-temperature" spectra /1, 2, 5/ is found. A similar temperature dependence is

observed in InP:Fe. Although the effect is less pronounced all seven lines (a' - e'), (a, b) show clearly the same behaviour as the corresponding resonances in GaP:Fe.



**Fig. 2:** Evolution of the (Fe<sup>2+</sup>, h) related lines in InP and GaP in the mK-range.

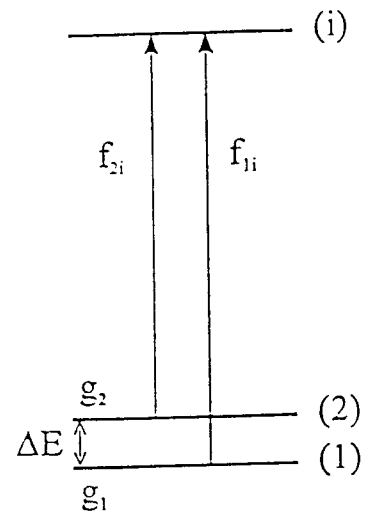
The change of the absorption intensities can be explained by thermalization effects in the ground state of the transitions [4]. Since the thermal energy  $E=kT$  is only a few  $\mu\text{eV}$  at mK temperatures the splitting of the ground state is smaller than the linewidth of the transition and each absorption line is the superposition of two spectrally unresolved lines (see Fig. 3). Therefore, the intensity of one transition is given by

$$I_i = \frac{A \cdot f_{ji}}{1 + \frac{g_2}{g_1} \cdot e^{-\Delta E/kT}} \left\{ 1 + \frac{f_{ji}}{f_{ji}} \cdot \frac{g_2}{g_1} \cdot e^{-\Delta E/kT} \right\} \quad (1)$$

where  $f_{ji}$  means the oscillator strength from the ground state to the final state,  $g$  is the degree of degeneracy and  $A$  represents the intensity at  $T=0\text{K}$ .

We determine a ground state splitting of  $15 \pm 3 \mu\text{eV}$  and  $8 \pm 2 \mu\text{eV}$  for GaP and InP, respectively. These values are in good agreement with the ground state splitting of the  $\text{Fe}^{3+}$  ( ${}^6\text{A}_1$ ) state determined by EPR [8] proving unambiguously that  $\text{Fe}^{3+}$  is the initial state of these transitions.

The results of temperature dependent absorption measurements of the (Fe<sup>2+</sup>, h)-associated lines are shown in Fig. 4. The intensity of each line (a' - e'), (a, b) is plotted as a function of temperature and full lines represent theoretical fits according to equation (1) with  $\Delta E=14.5 \mu\text{eV}$  and  $8.5 \mu\text{eV}$  for GaP and InP, respectively. The parameters used for the theoretical fits are summarized in Tab 1.



**Fig. 3:** Scheme of a system with a two-fold split ground state and one excited state.

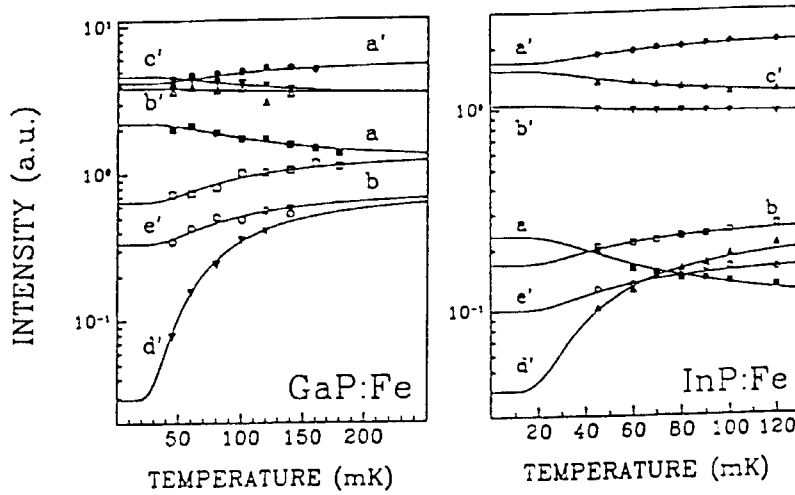


Fig.4:

Temperature dependence of the fine structure lines attributed to the formation of a  $(\text{Fe}^{2+}, h)$  bound state

InP:Fe	a'	b'	c'	d'	e'	a	b
$\Delta E$ ( $\mu\text{eV}$ )	8.5	8.5	8.5	8.5	8.5	8.5	8.5
$g_{\uparrow}/g_{\downarrow}$	2	2	2	2	2	2	2
$f_{\uparrow i}/f_{\downarrow i}$	1.52	0.8	0.5	9.2	2.3	<0.02	2
$A f_{\uparrow i}$	1.7	1.04	1.55	0.04	0.1	0.23	0.17

GaP:Fe	a'	b'	c'	d'	e'	a	b
$\Delta E$ ( $\mu\text{eV}$ )	14.5	14.5	14.5	14.5	14.5	14.5	14.5
$g_{\uparrow}/g_{\downarrow}$	2	2	2	2	2	2	2
$f_{\uparrow i}/f_{\downarrow i}$	1.6	0.8	0.5	>40	3	0.2	2.7
$A f_{\uparrow i}$	3.5	3.2	4.2	<0.03	0.3	2.2	0.6

Tab. 1

Parameters for the theoretical fits of the temperature dependencies which are shown in Fig.4.

#### IV. Discussion

Based on the temperature dependence not only the activation energy but also the ratio of the oscillator strengths of the transitions from the two ground states to one excited state can be deduced /4/. The relative oscillator strengths yield information about the final states and about the fine structure of the  $(\text{Fe}^{2+}, h)$  bound state. Comparing the results for both systems two facts have to be considered. First, all lines in InP and GaP behave in the same way and second, the temperature dependencies of  $a'$  and  $a$  as well as of  $b'$  and  $b$  are opposite to each other.

These results are incompatible with the assignment of the lines ( $a, b$ ) in GaP to phonon replicas of  $a'$  and  $b'$  /5/ since phonon replica show the same temperature dependence as the zero-phonon lines. Instead the doublet ( $a, b$ ) in GaP exhibits an analogue temperature behaviour as the lines ( $a, b$ ) in InP, which requires for a similar interpretation in both systems: the doublet ( $a, b$ ) in InP as well as in GaP is attributed to zero-phonon transitions into bound  $(\text{Fe}^{2+}, h)$  states, where the hole is in its first excited state. In GaP the weak absorption lines (?) appear due to a higher excited state of the hole.

A detailed investigation of the quintett ( $a' - e'$ ) shows a splitting of the components being smaller than the splitting of the  $\text{Fe}^{2+}(^5E)$  state by a factor of 2 and 2.4 in InP and GaP /1, 2/, respectively.

In a simple model this fact was explained in terms of a modified spin-orbit interaction /2/ where the localized hole influences the  $\text{Fe}^{2+}$  centre. This description in terms of a reduced spin-orbit interaction without any influence on the symmetries of the ( $\Gamma_i$ ,  $i=1..5$ )  $^5\text{E}$ -sublevels is insufficient since the temperature dependence of the  $a'$  and  $a$  as well as that of  $b'$  and  $b$  is inverted the final states must have different characters which cannot be explained in the simple model of a reduced spin-orbit interaction. A complete description of the experiment has to include the exchange interaction between the hole and the impurity centre.

The exchange interaction leads to a splitting of the unpertubated  $\text{Fe}^{2+}$  states and the final states are described by the product  $\Gamma_1 (^5\text{E}) \times \Gamma_8$ . For the quintett ( $a' - e'$ ) the influence of the exchange interaction is of the same order as of the spin-orbit interaction which manifests itself by the strong reduction of the fine structure splitting mentioned above. For the doublet ( $a, b$ ) the influence of the exchange interaction is less pronounced since the binding energy is smaller and the localization of the hole is weaker. However, even if the influence of the exchange interaction is weak the characters of the final states are completely changed as it must be the fact for the doublet ( $a, b$ ).

Nevertheless, the differences of the fine structure in both materials are remarkable and have to be discussed. Although the situation seems to be similar in both materials there is one significant discrepancy which may be able to give some important hints for the understanding of the spectra. The effective mass of the  $\Gamma_8$  valence band hole is larger in GaP than in InP reducing the radius of its wavefunction. As a result, the binding energy of an effective-mass acceptor is much larger in GaP (45.3meV) than in InP (35.2meV) /9/. Therefore the influence of the exchange interaction will be stronger in GaP than in InP. This fact manifests itself directly in the enhanced reduction of the ( $a' - e'$ ) splitting from 2 in InP to 2.4 in GaP and may be responsible for the different appearance of the fine structure lines in both materials.

## Conclusion

The temperature dependence of the narrow lines at the onset of the  $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$  charge transfer band in InP and GaP in the mK-range can be explained by thermalization effects in the initial state  $\text{Fe}^{3+}(^6\text{A}_1)$ . The characteristic temperature behaviour of the lines ( $a' - e'$ ) and ( $a, b$ ) is qualitatively the same in InP and GaP. Thus the electronic transitions have to be described in an analogous way in both systems. The exchange interaction between the hole and the  $\text{Fe}^{2+}$  ion has to be taken into account to explain the experimental results. In both materials InP:Fe and GaP:Fe the two series ( $a' - e'$ ) and ( $a, b$ ) are no-phonon lines due to the formation of a bound ( $\text{Fe}^{2+}, h$ ) complex where the hole is in its ground state  $1\text{S}_{3/2}$  or in the first excited state  $2\text{P}_{3/2}$ , respectively.

## References

- /1/ K. Thonke, K. Pressel, Phys. Rev B **44**, 13418 (1991)
- /2/ T. Wolf, D. Bimberg, W. Ulrici, Phys. Rev B **43**, 10004 (1991)
- /3/ A. Juhl, A. Hoffmann, D. Bimberg, H.-J. Schulz, Appl. Phys. Lett. **50**, 1292 (1987)
- /4/ L. Podlowski, T. Wolf, R. Heitz, A. Hoffmann, D. Bimberg, I. Broser, W. Ulrici, Proc. 21st Intern. Conf. Phys. Semicond, Beijing 1992, 1665
- /5/ K. Pressel et al., to be published in Phys. Rev. B
- /6/ D. Bimberg, T. Wolf, J. Böhrer, Advances in Nonradiative Processes in Solids, ed. by B. DiBartolo, Plenum Press, New York (1991), 577
- /7/ L. Podlowski, A. Hoffmann, I. Broser, J. Crystal Growth **117**, 698 (1992)
- /8/ H. H. Woodbury, G. W. Ludwig, Bull. Americ. Phys. Soc. **6**, 118 (1961)
- /10/ A. Baldereschi, N. Lipari, Phys. Rev. B **9**, 1525 (1974)