

PHOTOLUMINESCENCE OF Fe-COMPLEXES IN GaN

P. THURIAN, A. HOFFMANN, L. ECKEY, P. MAXIM, R. HEITZ, I. BROSER,
K. PRESSEL*, B.-K. MEYER**, J. SCHNEIDER***, J. BAUR***, M. KUNZER***
TU-Berlin, Institut für Festkörperphysik, Hardenbergstr. 36, 10623 Berlin, Germany
*Institut für Halbleiterphysik, P. O. Box 409, 15204 Frankfurt (Oder), Germany
**Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 16, D-35392 Giessen Germany
***Fraunhofer-Institut, Tullastr. 72, D-79108 Freiburg, Germany

ABSTRACT

We report a photoluminescence (PL) and photoluminescence excitation (PLE) investigation of the deep iron acceptor in hexagonal GaN. Codoped samples give rise to a new zero-phonon line (ZPL) at 1.268 eV. The spectral shape of its phonon side band is very similar to that of the Fe^{3+} -spectrum. A lifetime of 2.6 ms was measured for this ZPL which indicates a spin-forbidden transition. In contrast to isolated Fe^{3+} , no Zeeman-splitting is observed. PLE spectra of the Fe^{3+} (${}^4\text{T}_1$ - ${}^6\text{A}_1$) zero-phonon line at 1.299 eV in semi-insulating GaN samples reveal intracenter excitation processes via excited states of the Fe^{3+} center. Three excited Fe^{3+} crystal field states at 1.299 eV (${}^4\text{T}_1$), 2.01 eV (${}^4\text{T}_2$), and 2.731 eV (${}^4\text{E}$) above the ${}^6\text{A}_1$ ground state were identified. PLE spectroscopy for the 1.268 eV zero-phonon line reveals resonances at 2.3 eV and 2.65 eV. The 1.268 eV ZPL is tentatively attributed to a Fe-complex with a nearby donor.

INTRODUCTION

GaN and related alloy systems are very promising for applications as widegap LEDs and injection lasers¹, as well as for high-temperature electronics. The investigation of impurity, native-point or extended-defect properties is essential to optimize the device quality. However, only few studies of transition metals (TMs) exist. A luminescence band with a ZPL at 1.299 eV was unambiguously assigned to the Fe^{3+} (${}^4\text{T}_1$ - ${}^6\text{A}_1$) transition.^{2,3} Recently, detailed PLE data of isolated Fe^{3+} in GaN was presented and new excited states of the d^5 configuration were identified.^{4,5} Additionally, a new zero-phonon line (ZPL) at 1.268 eV was observed and tentatively attributed to Fe-related defects. The aim of this paper is to compare the properties of the isolated Fe^{3+} center and iron-related defect centers in GaN by means of PL and PLE spectroscopy. Special emphasis is put on PL studies in magnetic fields up to 15 T for identifying the electronic structure.

EXPERIMENTAL RESULTS

We investigated a series of hexagonal GaN samples epitaxially grown on (0001) sapphire. Results presented in this paper are obtained from a 400 μm thick n-type sample (crystal 1) and a 38 μm thick semi-insulating sample doped with Fe (crystal 2). Luminescence was excited by various lines of an Ar^+ -, Kr- or a HeCd-laser. The Zeeman PL experiments are carried out using a superconducting 15 T magnet built in split-coil configuration. Depending on the spectral region the excitation source in PLE measurements was either a xenon lamp or a tungsten-halogen lamp, spectrally dispersed by a 0.35 double-grating monochromator. The luminescence was detected by a cooled Ge photodiode. We employed a double-prism monochromator to control the detection window in the PLE experiments. High-resolution PLE experiments were performed using a dye laser as tunable excitation source.

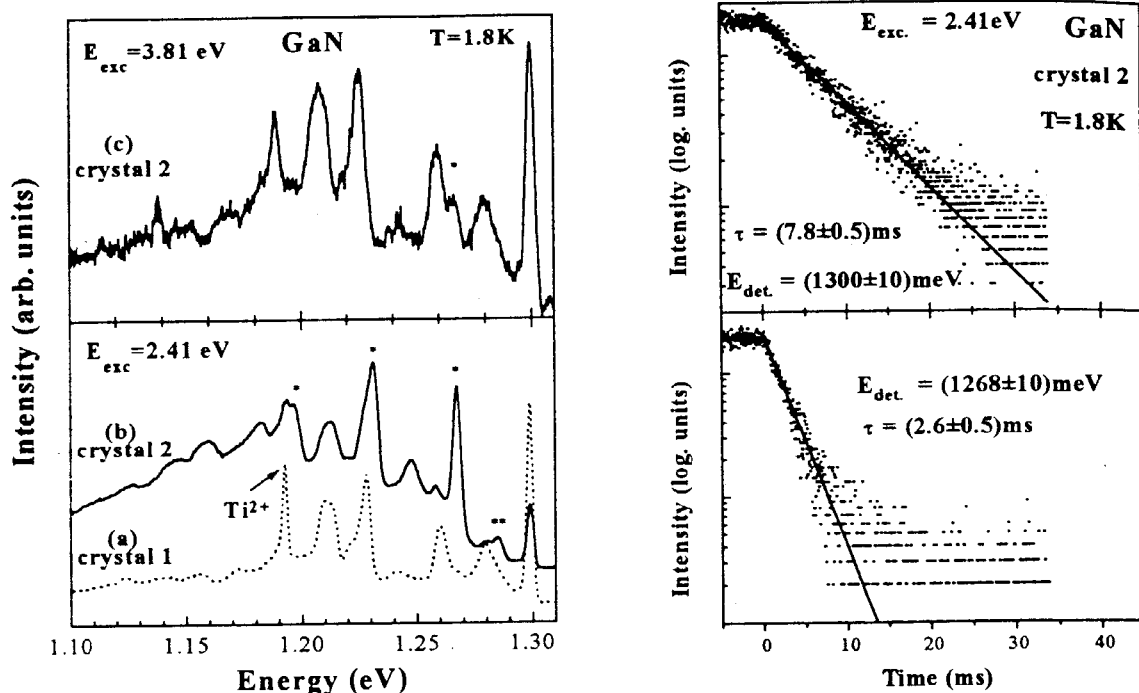


Figure 1: (left) Low-temperature PL of the Fe^{3+} (${}^4T_1-{}^6A_1$) center. Shown are the n-type crystal 1 (a) and the semiinsulating sample 2 (b,c). Spectra (a) and (b) were recorded using the green Ar^+ -laser line at 2.412 eV for excitation. New ZPLs at 1.268 eV and 1.286 eV are observed in the semiinsulating sample and tentatively attributed Fe -related defect complexes. These lines and the corresponding phonon replica are labeled by * and **, respectively. (right): Decay of the 1.299 eV ZPL and of the 1.268 eV ZPL.

PL Results

Figure 1 represents typical PL spectra of the Fe^{3+} (${}^4T_1-{}^6A_1$) luminescence for different excitation energies. Exciting the sample at 2.412 eV new ZPLs at 1.268 eV and 1.286 eV are observed (indicated by * and **), superimposed to the luminescence of isolated Fe^{3+} with its ZPL at 1.299 eV. The full width at half maximum (FWHM) of the 1.268 eV ZPL is 3 meV whereas for the 1.299 eV line the FWHM is only 1 meV. A lifetime of 7.8 ± 0.5 ms and 2.6 ± 0.5 ms is detected for the 1.299 eV and 1.268 eV ZPL, respectively. These lifetimes in the ms range are typical for spin-forbidden transitions. Temperature dependent PL experiments reveal the detection of additional ZPLs on the high-energy side of the respective ZPL due to the thermal population of higher excited fine-structure states. For the 4T_1 state of isolated Fe^{3+} these three states are 1.8, 2.6 and 3.8 meV above the lowest component at 1.2988 eV. For the 1.2687 eV ZPL these states are 2.0 and 3.5 meV above the lowest component. In order to obtain insight into the spectral shape of both superimposed luminescence bands we have to separate the PL of the new ZPLs from the PL of isolated Fe^{3+} . Therefore we normalize the intensity of the 1.299 eV ZPL of isolated Fe^{3+} in the spectra c and b of figure 1 and subtract both normalized spectra. The result is shown in curve a of figure 2. The vibronic structure of the 1.268 eV ZPL (spectrum a) looks quite similar to that of Fe^{3+} luminescence band (spectrum b)

ZPL. However, the relative intensity and the energy difference of the vibronic peaks to each ZPL vary slightly. Thus, different local vibrational modes are involved for both defects.⁶

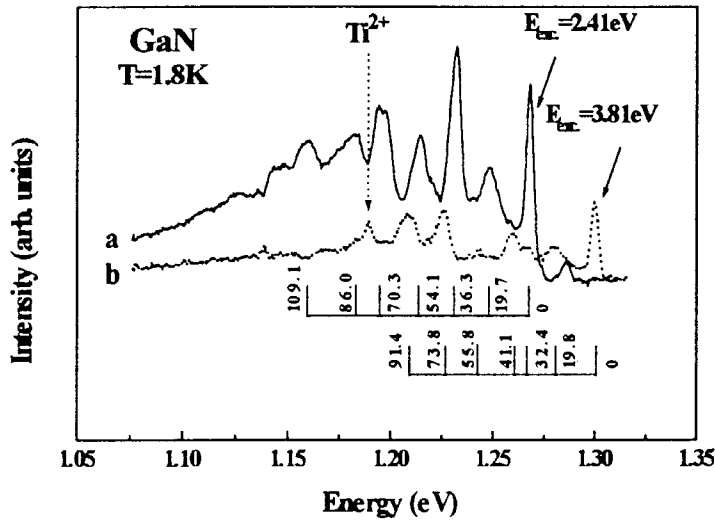


Figure 2: PL-spectrum of the 1.268 eV luminescence (a) in comparison to the Fe^{3+} luminescence (b) of the semiinsulating GaN sample 2. The energy differences of the vibronic peaks to the respective ZPL are given in meV.

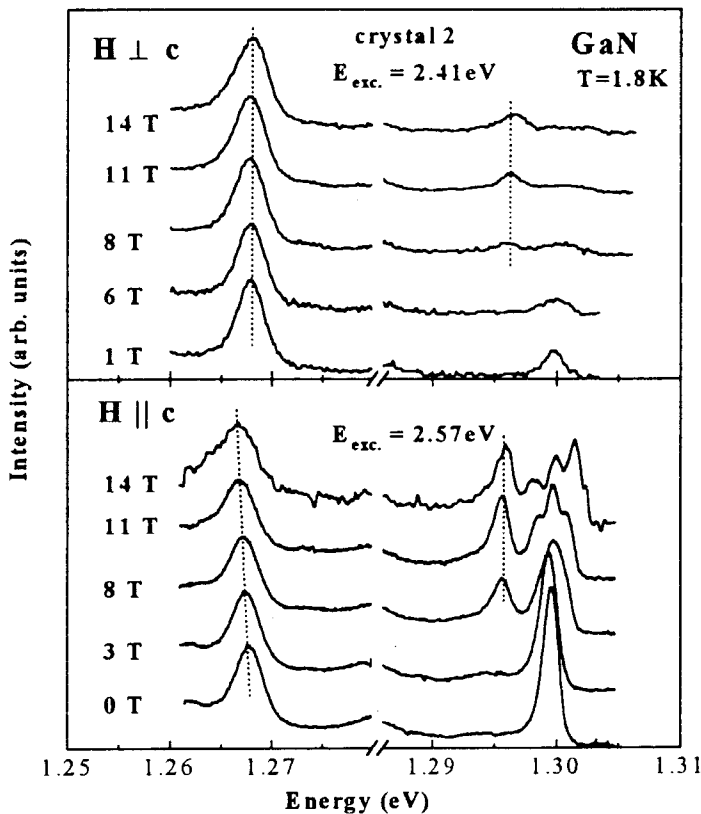


Figure 3: Zeeman spectra of the ZPL-region in the configuration $H \perp c$ and $H \parallel c$ for $T = 1.8$ K. For $H \parallel c$ the crystal is excited at 2.57 eV, whereas for $H \perp c$ the crystal is excited at 2.41 eV. No Zeeman-splitting is observed for the 1.268 eV ZPL. With increasing magnetic field, a new ZPL at 1.296 eV is observed for both configurations. The relative intensity change between the 1.299 eV ZPL and the 1.268 eV ZPL in both Zeeman configurations is due to the different excitation behavior of the ZPLs.

In order to get insight in the electronic structure of the defect, we performed Zeeman spectroscopy of the ZPL region. For $H \parallel c$, the three components³ of the Fe^{3+} ZPL are well resolved above $B=11$ T. In contrast to the Fe^{3+} behavior, no Zeeman-splitting is observed for the 1.268 eV ZPL. Only a slight shift to lower energies of $61 \pm 5 \mu\text{eV/T}$ is observed in this configuration. For $H \perp c$ the sixfold splitting³ of the Fe^{3+} ZPL is not resolved, but a broadening

with increasing magnetic field is observed. The 1.268 eV ZPL does not show any shift or broadening in this configuration. This indicates that the electronic structure of the Fe-related defect is strongly modified by the nearby impurity atom. The relative intensity change between the 1.299 eV ZPL and the 1.268 eV ZPL in both Zeeman configurations is due to the different excitation behavior of the ZPLs.

Additionally, a new ZPL at 1.296 eV is observed with increasing magnetic field for both Zeeman configurations. The excitation behavior of this line is similar to that of isolated Fe^{3+} . This line is also specific for the Fe-doped crystal 2 and was not observed for GaN epilayers grown on SiC.³ This might indicate that the Fe-doping is responsible for this line. If we explain this line by ferromagnetic coupling between two nearby iron atoms⁷, we should expect a fast decay within the ground state, because the spin-selection rule is lifted. More investigations have to be done to clarify the origin of this new ZPL.

PLE Results

The presence of PL from Fe complexes renders the spectral position and the width of the detection window critical for the reliability of the PLE experiments. Spectrum (a) in Figure 4 presents the PLE of isolated Fe^{3+} detecting only luminescence in a 10 meV window around 1.299 eV. The excitation behavior of the Fe^{3+} luminescence depends critically on the stable charge state of iron. The spectra of semi-insulating samples show structured absorption bands not observed for the n-type samples (c).

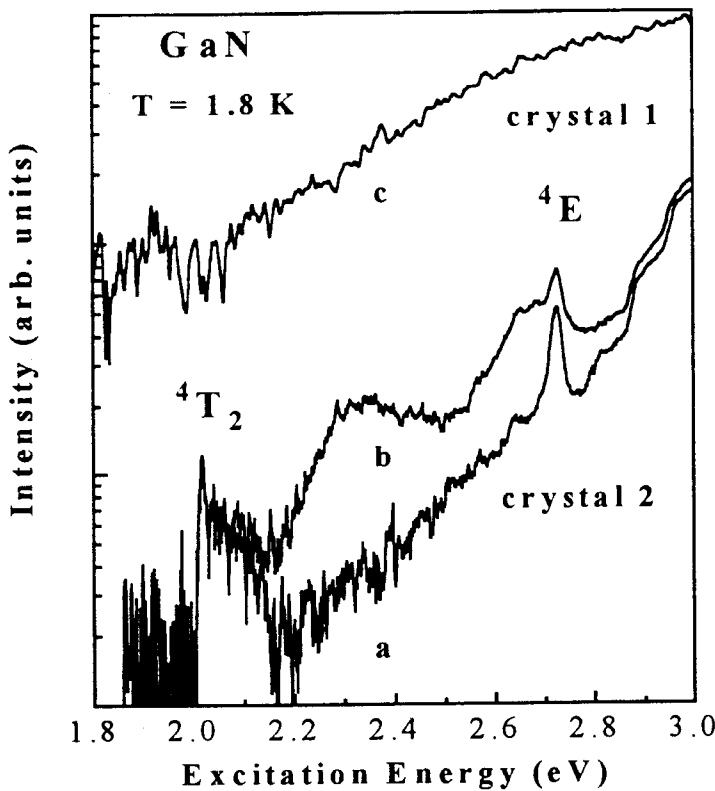


Figure 4: Low-temperature PLE spectra of the Fe^{3+} (${}^4T_1-{}^6A_1$) luminescence for the two samples. Crystal 1 is n-type containing Fe^{2+} (spectrum c). Crystal 2 contains practically only Fe^{3+} (spectra a and b). Luminescence in a 10 meV window around the ZPL at 1.299 eV was detected for spectra a and c, whereas the detection energy is 1.268 eV for the spectrum b.

For the semi-insulating sample, fine structure is resolved around 2.0 eV and 2.8 eV and a broad excitation band appears in the uv spectral region (Fig. 4 (a)). The occurrence of sharp ZPLs in

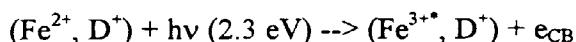
the PLE spectrum of the Fe^{3+} luminescence together with the Fe^{3+} EPR signal in the crystal directly demonstrates the presence of the neutral $3+$ charge state in the unexcited samples.

Using a dye laser as tunable excitation source at least four ZPLs (at 2.0091 eV, 2.0152 eV, 2.0170 eV, and 2.0188 eV) are resolved with FWHM down to 1.2 meV. Transitions into higher excited quartet states are known to lead to structured bands in PLE spectra of the ${}^4\text{T}_1$ - ${}^6\text{A}_1$ luminescence. This was experimentally verified for Mn^{2+} in ZnS.⁸ Thus, we attribute the 2.01 eV absorption band to the ${}^6\text{A}_1$ - ${}^4\text{T}_2$ transition of Fe^{3+} . The structure at 2.8 eV starts with a single ZPL at 2.731 eV. The energy separation between this ZPL and the first step amounts to 157 meV and, thus, corresponds neither to the step period of 75 meV nor to typical phonon modes of hexagonal GaN. Therefore, we treat the 2.731 eV absorption as a separate feature and tentatively attribute it to an intracenter transition involving the next excited quartet state, the ${}^6\text{A}_1$ - ${}^4\text{E}$ transition. From our results we conclude that the crystal field splitting of the ${}^4\text{G}$ multiplet of Fe^{3+} in GaN is approximately three times larger than that of Mn^{2+} in II-VI compounds. This strong crystal field may be the result of the comparatively small lattice constant of GaN, of the $3+$ charge state of iron, and of the high electronegativity of nitrogen.

The spectral appearance of the step-like PLE structure showing at least four replica with increasing intensity is unusual for an intracenter transition of a TM. However, it is rather typical for deeply bound excitons or deeply bound electron-hole pairs.^{9,10} The steps are located on the low-energy onset of the broad UV excitation band, which we assign to the $\text{Fe}^{3+/2+}$ charge-transfer transition. We therefore attribute this structure to the formation of a shallow bound state at the Fe center. The exact location of the $\text{Fe}^{3+/2+}$ acceptor level in GaN is not clear yet. The observation of the $\text{Fe}^{3+/2+}$ charge-transfer band in PLE should provide this information. However, the superposition of shallow bound states of TMs to the low-energy slope of a charge-transfer band makes a fit of the ionization band difficult in order to determine the onset energy. But it seems reasonable to identify the energy (3.17 ± 0.10 eV) at which the step-like structure vanishes and the broad structureless charge-transfer band begins to dominate with the energy position of the $\text{Fe}^{3+/2+}$ acceptor level. This assignment yields a binding energy of (280 ± 100) meV for the shallow bound state of the isolated Fe center in GaN. This complex is also an excited state of Fe^{3+} and relaxes nonradiatively to the ${}^4\text{T}_1$ state. Due to the position of the deep $\text{Fe}^{3+/2+}$ acceptor level close to the conduction band, hybridization of the core states of Fe is more important than in the other III-V compounds. Together with the high binding energy, these effects add up to a strong exchange interaction between the core hole and the bound hole. Therefore, a deeply bound electron-hole complex ($\text{Fe}^{3+}, \text{e}, \text{h}$) is the appropriate description of this state. A very similar situation was demonstrated for shallow bound states of Ni comparing cubic ZnS and hexagonal CdS.⁹ Recent calculations¹⁰ show that the hybridization of the TM ground state with band-states is favored in hexagonal host crystals. Indeed, all known shallow states of TMs in wurtzite crystals have the character of a (TM, e, h) complex.

Compared to the Fe^{3+} PLE in n-type and semiinsulating samples, two additional features peaking at 2.3 eV and 2.65 eV are observed in the PLE spectrum of the 1.268 eV ZPL. (spectrum b). The 2.65 eV resonance is rather broad in comparison with the 2.73 eV PLE resonance of Fe^{3+} . This broadening can be caused by the larger energy separation within the ${}^4\text{E}$ state of the Fe^{3+} complex due to the larger crystal field. A similar observation was made for Mn^{2+} centers in cubic ZnS.¹¹ Here, additional axial crystal fields due to polytype effects or nearby impurity atoms cause a larger energy separation within the ${}^4\text{E}$ -state of the d^5 configuration of Mn^{2+} . The other additional feature is a broad PLE structure peaking at 2.3 eV. The peak energy of 2.3 eV agrees well with the expected $\text{Fe}^{2+/3+}$ low energy threshold of 2.36 eV within the ${}^4\text{T}_2$ state of isolated Fe^{3+} .⁵ This indicates that the other atom within the Fe complex might be a nearby

donor, resulting in a $(\text{Fe}^{2+}, \text{D}^+)$ complex in the unexcited crystal. The 1.268 eV PL of the Fe-complex is excited via a charge-transfer process of the Fe^{2+}



followed by the radiative relaxation of the excited $(\text{Fe}^{3+}, \text{D}^+)$ center causing the 1.268 eV luminescence and the (very slow) capture of the electron.

CONCLUSION

The similar spectral shape of the vibronic sideband and the energy position together with the decay time indicate the close correlation between the isolated Fe^{3+} (${}^4\text{T}_1\text{-}{}^6\text{A}_1$) transition at 1.299 eV and the 1.268 eV defect. Additionally, the PLE results can be explained in the Fe term-scheme. On the basis of these observations, the 1.268 eV is tentatively attributed to radiative recombination within a $(\text{Fe}^{3+}, \text{D}^+)$ defect. However, the Zeeman-behavior of the 1.268 eV ZPL do not show the clear fingerprint of the d^5 -configuration. This indicates, that the electronic structure of the 1.268 eV transition is strongly modified by the nearby impurity atom.

REFERENCES

1. S. Nakamura, Jpn. J. of Appl. Phys. 35 (1996) L74
2. K. Maier M. Kunzer, U. Kaufmann, J. Schneider, H. Amano, I. Akasaki, T. Detchprohm, K. Hiramatsu, Mat. Science Forum 143-147 (1994) 93
3. R. Heitz, P. Thurian, I. Loa, L. Eckey, A. Hoffmann, I. Broser, K. Pressel, B. K. Meyer, E. N. Mokhov, Appl. Phys. Lett. 67 (19) (1995) 2822
4. P. Thurian, R. Heitz, L. Eckey, P. Maxim, V. Kutzer, A. Hoffmann, I. Broser, K. Pressel, B.-K. Meyer, Proc. of the 23th ICPS 1996, Berlin, Ed. M. Scheffler, R. Zimmermann, World Scientific pp. 2897-2901
5. R. Heitz, P. Maxim, L. Eckey, P. Thurian, A. Hoffmann, I. Broser, K. Pressel, B.-K. Meyer, Phys. Rev. B, accepted
6. P. Thurian, G. Kaczmarczyk, H. Siegle, R. Heitz, A. Hoffmann, I. Broser, B.-K. Meyer, R. Hoffbauer, U. Scherz
Mat. Science Forum, Vol. 196-201 (1995) 1571
7. J. Kreissl, W. Gehlhoff, Phys. Status Solidi A 81 (1984) 701
8. R. Parrot, A. Geoffroy, C. Naud, W. Busse, H.-E. Gumlich, Phys. Rev. B 23 (1981) 5288
9. R. Heitz, A. Hoffmann, I. Broser, Phys. Rev. B 48 (1993) 8672
10. P. Dahan, V. Fleurov, K. A. Kikoin, Mat. Science Forum 196-201 (1995) 755
11. U. W. Pohl, H.-E. Gumlich, Phys. Rev. B, 40 (1989) 1194