

Fe-RELATED DEFECTS IN GaN EPILAYERS

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We report a comprehensive photoluminescence (PL) and photoluminescence excitation (PLE) investigation of the deep iron acceptor in hexagonal GaN. PLE spectra of the Fe^{3+} (${}^4\text{T}_1$ - ${}^6\text{A}_1$) luminescence in semi-insulating GaN samples reveal intracenter excitation processes via excited states of the Fe^{3+} center. We identify three excited Fe^{3+} crystal field states located 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. A step-like excitation structure on the low-energy onset of the $\text{Fe}^{3+/2+}$ charge-transfer band is attributed to the formation of a (Fe^{3+} ,e,h) complex at 2.888 eV. Codoped samples give rise to a new PL zero-phonon line at 1.268 eV. The spectral shape of its phonon side band is very similar to that of the Fe^{3+} -spectrum. On the basis of time-resolved spectroscopy and PLE this ZPL is attributed to a Fe-complex with a nearby donor.

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 zero-phonon line (ZPL) at 1.299 eV was unambiguously assigned to the Fe^{3+} (${}^4\text{T}_1$ - ${}^6\text{A}_1$) transition.^{2,3} The aim of this paper is to investigate the excited states of the isolated Fe^{3+} center and iron-related defect centers by means of PL and PLE spectroscopy.

1 Experimental results and discussion

We investigated a series of hexagonal GaN samples epitaxially grown on (0001) sapphire. Results presented in this paper are obtained from a semi-insulating sample doped with Fe and from a n-type sample. Luminescence was excited by various lines of an Ar⁺- or a HeCd-laser. 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. Figure 1 represents typical PL spectra of the Fe^{3+} (${}^4\text{T}_1$ - ${}^6\text{A}_1$) luminescence for different excitation energies. Exciting below the band gap at 2.412 eV new ZPLs at 1.268 eV and 1.286 eV are observed, 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. The energy shift of the phonon sideband and the relative intensity ratio with respect to the

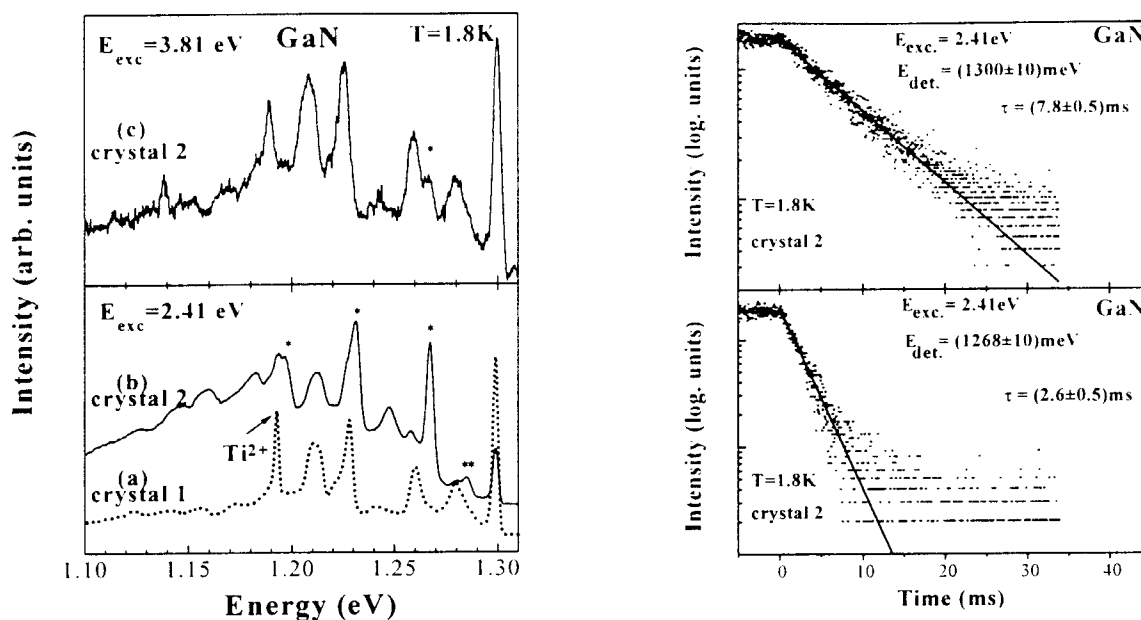


Figure 1: (left) Low-temperature PL of the Fe^{3+} (${}^4\text{T}_1\text{-}{}^6\text{A}_1$) center. Shown are the n-type crystal (a) and the semiinsulating sample (b,c). Spectra (a) and (b) were recorded using the green Ar-laser line at 2.412 eV for excitation. New ZPLs at 1.268 eV and 1.286 eV are observed 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.

ZPLs is quite similar for both luminescence bands. Additionally, 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 ${}^4\text{T}_1$ 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. Altogether, this indicates similar electronic and vibronic properties for both luminescence centers and leads to the tentative conclusion, that the 1.268 eV luminescence belongs to an Fe^{3+} related defect complex.

1.1 PLE of the 1.299 eV ZPL

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. Figure 2 presents the PLE spectra 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.

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. 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

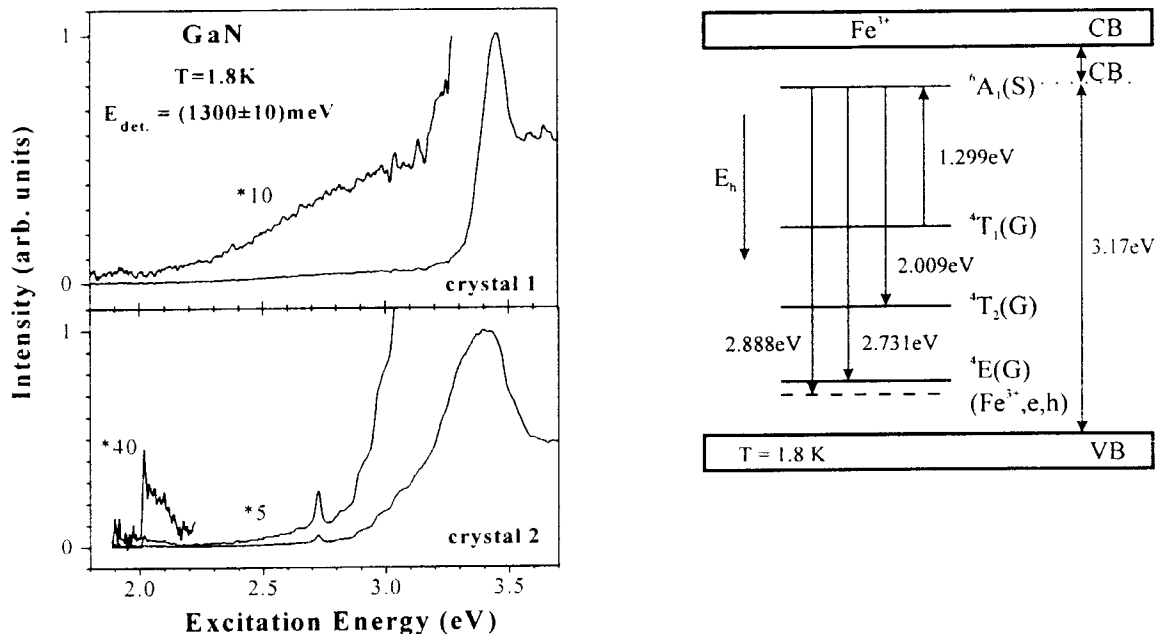


Figure 2: (left) Low-temperature PLE spectra of the Fe^{3+} (${}^4\text{T}_1$ - ${}^6\text{A}_1$) luminescence for the two samples. Crystal 1 is n-type containing Fe^{2+} . Crystal 2 contains practically only Fe^{3+} . Luminescence in a 10 meV window around the ZPL at 1.299 eV was detected.

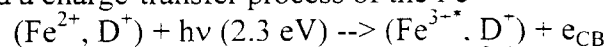
(right) Energy levels of the Fe^{3+} center in hexagonal GaN in the hole picture.

the ${}^4\text{T}_1$ - ${}^6\text{A}_1$ luminescence. This was experimentally verified for Mn^{2+} in ZnS .⁴ 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.^{5,6} 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.⁵ Recent calculations⁶ 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.

1.2 PLE of the 1.268 eV ZPL

The shown PLE fine structure is only resolved detecting the 1.299 eV luminescence and does not appear detecting the 1.268 eV luminescence. Only a broad PLE structure peaking at 2.3 eV is observed. The spectrum is very similar to the Fe^{3+} PLE-spectra in n-type samples. This indicates, that the other atom within the Fe complex is a nearby donor, resulting in a $(\text{Fe}^{2+}, \text{D}^+)$ complex in the unexcited crystal. The 1.268 eV PL of the Fe^{3+} complex is excited via a charge-transfer process of the Fe^{2+}



followed by the radiative relaxation of the excited Fe^{3+*} center within the complex causing the 1.268 eV luminescence and the (very slow) capture of the electron. 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+} .

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