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Excited states of Fe^{3+} in GaN

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We report a comprehensive photoluminescence excitation (PLE) investigation of the deep iron acceptor in hexagonal GaN. PLE spectra of the Fe^{3+} $[{}^4T_1(G)\text{-}{}^6A_1(S)]$ luminescence in semi-insulating GaN samples reveal intracenter excitation processes via excited states of the Fe^{3+} center. Zero-phonon lines resolved around 2.01 and at 2.731 eV are attributed to the ${}^6A_1(S)\text{-}{}^4T_2(G)$ and the ${}^6A_1(S)\text{-}{}^4E(G)$ transition, respectively. A steplike excitation structure on the low-energy onset of the $Fe^{3+/2+}$ charge-transfer band is attributed to the formation of a (Fe^{3+},e,h) complex at 2.888 eV. We estimate a binding energy of 280 meV locating the deep $Fe^{3+/2+}$ acceptor level 3.17 eV above the valence-band maximum. In n-type GaN samples the Fe^{3+} luminescence is excited by hole-transfer processes. The experimental results indicate that the internal reference rule fails for the GaN/GaAs heterostructure. [S0163-1829(97)00807-2]

I. INTRODUCTION

Group-III nitrides gain increasing interest in view of their potential for optoelectronic devices operating in the visible and ultraviolet spectral region. Efficient blue and green light-emitting diodes[1] are now commercially available and the first electrically pumped laser diode has been demonstrated.[2,3] Despite this enormous progress in growth and device technology there is only little information about deep defects in these materials. Transition metals (TM's) form deep defects and can be expected to be common contaminations of the group-III nitrides which are grown at very high temperatures. Even though their technological relevance for growing high-resistivity material was already demonstrated for Fe- and Cr-doped GaN layers decades ago,[4] the first detailed information on TM defects was reported only recently.[5–14]

A structured near-infrared luminescence band was observed in hexagonal GaN (Ref. 5) which is dominated by a zero-phonon line (ZPL) at 1.299 eV. Optically detected magnetic-resonance spectra recorded on this luminescence band at 1.3 eV reveal the fingerprint of a ${}^6A_1(S)$ state of an electronic d^5 configuration.[6] Zeeman experiments clearly prove that the ${}^6A_1(S)$ state is the ground state involved in the ZPL transition.[10] Thus, the 1.3-eV luminescence is attributed to the ${}^4T_1(G)\text{-}{}^6A_1(S)$ luminescence of Fe^{3+} which is supported by the long lifetime of 8 ms and the characteristic fine structure of the excited state.[5,10] Baur *et al.*[7,8] reported photoluminescence excitation (PLE) results and proposed the deep $Fe^{3+/2+}$ acceptor level to be 2.5 and 3.0 eV above the valence-band maximum in GaN and AlN, respectively. However, neither the detection conditions nor details of the investigated samples and the stable charge state of iron were given. Thus, the interpretation of the spectra given is questionable in view of the far reaching consequence of allocating the $Fe^{3+/2+}$ acceptor level. For transition metals in III-V and II-VI semiconductors a close correlation between the variation of the energy position of a deep TM level and the band offsets between the respective hosts has been found which is called the internal reference rule.[15,16] The determination of deep TM levels according to this rule was proposed to give experimental access to band offsets. Valence-band offsets between GaN, AlN, and several other materials were given based on the internal reference rule and the identification of the $Fe^{3+/2+}$ acceptor level in these materials.[7,8]

In this paper we report a comprehensive PLE investigation of the Fe^{3+} luminescence in n-type and semi-insulating GaN. We observe several excited states of the Fe^{3+} center as well as a bound state connected with the acceptor type $Fe^{3+/2+}$ charge-transfer transition. The $Fe^{3+/2+}$ acceptor level is found to be close to the conduction band. The impact on the applicability of the internal reference rule for GaN will be discussed below.

II. EXPERIMENT

We investigate a series of hexagonal GaN samples. They are GaN layers epitaxially grown on (0001) sapphire. We will present the results obtained from three typical samples containing Fe in different charge states. Crystal 1 is a 400-μm-thick epilayer grown by hydride vapor phase epitaxy.[17] The carrier concentration of this n-type crystal is 8×10^{16} a.u.$^{-3}$ at room temperature. Crystal 2 is 4 μm thick and was grown by metal organic chemical vapor deposition. The semi-insulating crystal 3 is 38 μm thick and grown by vapor phase epitaxy. This crystal was iron doped during growth.[4] The Fe^{3+} EPR signal can be observed in the dark for the crystals 2 and 3 confirming the semi-insulating character of these two samples. The transition-metal impurities are incorporated as unintentional dopants in the crystals 1 and 2. In addition to the Fe^{3+} luminescence the 1.19-eV luminescence

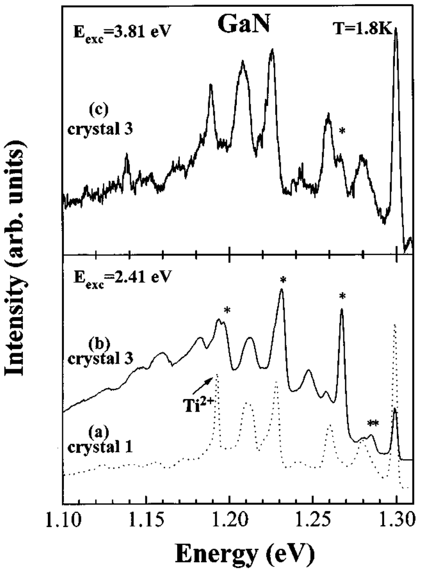

FIG. 1. Low-temperature photoluminescence of the Fe^{3+} $[^4T_1(G)\text{-}^6A_1(S)]$ center. Shown are the n-type crystal 1 (a) and the semi-insulating sample 3 (b,c), Spectra (a) and (b) were recorded using the green Ar-laser line at 2.412 eV for excitation. For spectrum (c) crystal 3 was excited at 3.81 eV. Exciting at 2.412 eV ZPL's at 1.268 and 1.286 eV are observed in the semi-insulating sample and are tentatively attributed to Fe-related defect complexes. These lines and the corresponding phonon replica are labeled by "*" and "**," respectively.

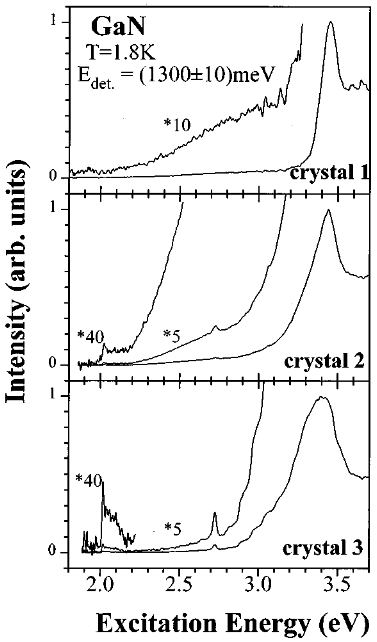

FIG. 2. Low-temperature PLE spectra of the Fe^{3+} $[^4T_1(G)\text{-}^6A_1(S)]$ luminescence for the three samples. Crystal 1 is an n-type containing Fe^{2+}. In crystal 2 both Fe^{2+} and Fe^{3+} are present, and crystal 3 contains practically only Fe^{3+}. Luminescence in a 10-meV window around the ZPL energy of 1.299 eV was detected.

can be observed in these three samples. This luminescence was attributed to Cr^{4+} (Ref. 5) and Ti^{2+} (Ref. 12) as well. For our optical experiments the samples were immersed in superfluid helium at 1.8 K. 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 (UV) or a tungsten-halogen lamp (visible to near infrared), spectrally dispersed by a 0.35-m double-grating monochromator. The luminescence was detected by a cooled Ge photodiode. We employed a double prism monochromator as a variable bandpass in order to control the detection window. A tunable dye laser in conjunction with a grating monochromator for detection was used for high-resolution PLE and selectively excited luminescence measurements.

III. RESULTS

For the above band-gap excitation, the spectra of all our GaN samples exhibit the 1.3-eV luminescence band. This indicates that Fe is a general contamination of the crystals. The observed shape of the band agrees with that reported recently for the Fe^{3+} $[^4T_1(G)\text{-}^6A_1(S)]$ luminescence.[5,9] The Fe^{3+} luminescence is shown in Figs. 1(b) and 1(c) for the semi-insulating sample 3, but is representative of all the samples investigated. Exciting below the band gap at 2.412 eV only n-type samples show this luminescence with high intensity [Fig. 1(a)], whereas semi-insulating samples exhibit additional luminescence bands under these excitation conditions [Fig. 1(b)]. The intensive ZPL at 1.268 eV is shifted to lower energies with respect to that of the Fe^{3+} $[^4T_1(G)\text{-}^6A_1(S)]$ band and a different fine structure appears in the phonon sideband. The defects involved may be Fe-related complexes. Details about this luminescence and its PLE characteristics will be reported in a forthcoming paper. The presence of this additional luminescence superimposing the Fe^{3+} $[^4T_1(G)\text{-}^6A_1(S)]$ makes the spectral position and the width of the detection window a deciding criterion for the reliability of the PLE experiments described below.

The excitation behavior of the Fe^{3+} luminescence depends essentially on the stable charge state of iron in the sample. Figure 2 compares the PLE spectra of the Fe^{3+} luminescence for the three crystals detecting only luminescence in a 10-meV window around the ZPL at 1.299 eV. For the semi-insulating crystals 2 and 3 even slightly lower detection energies give rise to additional excitation bands in the visible spectral region which are related to the Fe^{3+} complex luminescence [Fig. 1(b)]. n-type samples (crystal 1) show a weak structureless excitation band in the visible region with a low-energy onset at approximately 2.2 eV and high excitation efficiency in the near-band-gap region. The spectra of semi-insulating samples (crystals 2 and 3) show structured absorption bands not observed for the n-type samples. Fine structure is resolved around 2.01 and 2.73 eV and a broad excitation band appears in the UV spectral region. The PLE fine structure shown is only resolved detecting the Fe^{3+} $[^4T_1(G)\text{-}^6A_1(S)]$ luminescence and does not appear when detecting the 1.268-eV luminescence. The occurrence of sharp ZPL's in the PLE spectrum of the Fe^{3+} luminescence together with the Fe^{3+} EPR signal in crystals 2 and 3 directly demonstrates the presence of the neutral 3+ charge state in the unexcited samples which supports the semi-insulating character of both crystals. The ZPL's must be explained by intracenter excitation processes of Fe^{3+}.

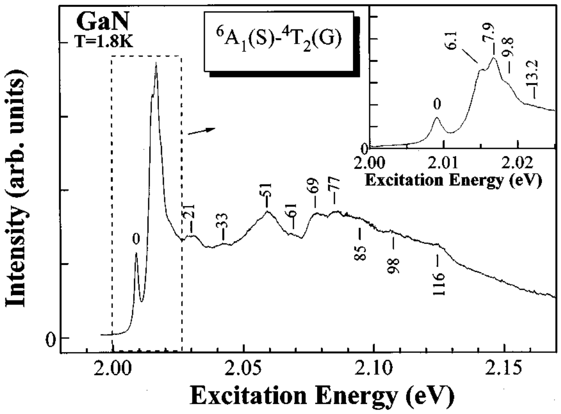

FIG. 3. Laser PLE spectrum of sample 3 in the region of the Fe^{3+} $[^6A_1(S)$-$^4T_2(G)]$ transition at 1.8 K. The inset gives the ZPL region over an enlarged energy scale. Luminescence in a 10-meV window around the ZPL position of 1.299 eV was detected. Energy shifts with respect to the ZPL at 2.0091 eV are given in meV.

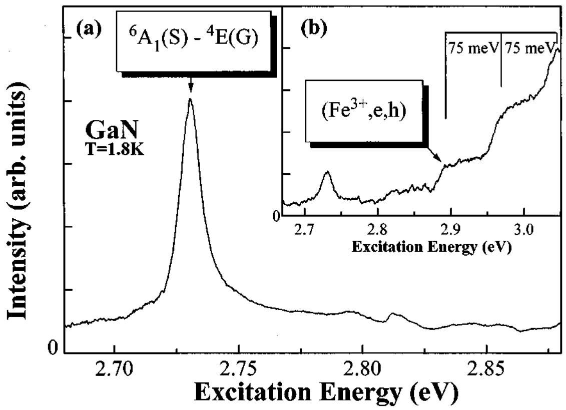

FIG. 4. High-resolution PLE spectrum of crystal 3 recorded at 1.8 K showing the Fe^{3+} $[^6A_1(S)$-$^4E(G)]$ transition and the (Fe^{3+},e,h) complex on the low-energy onset of the $Fe^{2+/3+}$ charge-transfer band. Luminescence in a 10-meV window around the ZPL position of 1.299 eV was detected.

Figure 3 shows a high-resolution spectrum of the intracenter excitation band at 2.01 eV of crystal 3, which was excited by a tunable dye laser. We were not able to resolve these PLE resonances for the n-type sample 1. Luminescence spectra excited at the various PLE fine structures show the typical Fe^{3+} luminescence which proves that all belong to the Fe^{3+} center. The set of ZPL's around 2.01 eV is followed by a vibronic sideband. The labels in Fig. 3 give the respective energy differences (in meV) between peaks in the sideband and the ZPL at 2.0091 eV. This vibronic sideband shows no distinct replica due to optical-phonon modes of hexagonal GaN.[18] Only a weak step around 69 meV almost coincides in energy with the E_2 (high) mode which dominates the sideband of the $^4T_1(G)$-$^6A_1(S)$ luminescence [Fig. 1(a)]. The inset of Fig. 3 shows the ZPL region over an enlarged energy scale. At least four ZPL's (at 2.0091, 2.0152, 2.0170, and 2.0188 eV) are resolved with full widths at half maximum (FWHM) down to 1.2 meV. Transitions into higher excited quartet states are known to lead to structured bands in PLE spectra of the $^4T_1(G)$-$^6A_1(S)$ luminescence.[19] Thus, we attribute this 2.01-eV absorption band to the $^6A_1(S)$-$^4T_2(G)$ transition of Fe^{3+}. The $^4T_2(G)$ is the quartet state next to the luminescent $^4T_1(G)$ state. The series of weak and broad peaks in the sideband of the 2.01-eV absorption indicates a dynamical Jahn–Teller effect in the excited state.

For the narrow band gap III-V semiconductors no optical transitions involving higher excited quartet and doublet states of Fe^{3+} have been reported,[20–22] indicating that they are degenerate with the valence band. Obviously, for GaN the $Fe^{3+/2+}$ acceptor level lies high enough in the band gap to allow the observation of higher excited crystal-field states in the band gap. The $^4T_2(G)$ state is expected to show a strong Jahn-Teller coupling to ε-type modes which can reduce the fine structure to a doublet. This was verified experimentally for Mn^{2+} in ZnS.[19] In hexagonal host crystals, however, the lower defect symmetry stabilizes the Fe^{3+} center against the Jahn-Teller coupling as recently established for the $^4T_1(G)$ state in ZnS, ZnO, and also GaN.[10,23,24] A similar effect on the $^4T_2(G)$ state in GaN would explain the richer fine-structure spectrum observed for the 2.01-eV absorption (inset of Fig. 3). A detailed assignment of the observed fine structure, however, requires more experimental data.

Figure 4 shows the fine structure observed for the semi-insulating sample 3 around 2.8 eV over an enlarged energy scale. The observed linewidths are not limited by the experimental resolution even for lamp excitation, but rather from the limited crystal quality. The PLE fine structure shown is only resolved detecting the Fe^{3+} $[^4T_1(G)$-$^6A_1(S)]$ luminescence and does not appear detecting the 1.268-eV luminescence. The structure starts with a single ZPL at 2.731 eV with a FWHM of 16 meV which is followed by a series of steplike resonances. The step period of approximately 75 meV almost corresponds to TO modes of hexagonal GaN $[E_{\mathrm{TO}}(\Gamma)=70.5\ \mathrm{meV}]$.[18] However, it is more likely that local vibrational modes of the Fe center are involved. This would explain the energy difference between the phonon energy and the step period.[25] Additionally, it is questionable whether the steplike structure can be interpreted as a phonon sideband of the intense ZPL at 2.731 eV. The energy separation between this ZPL and the first step amounts to 157 meV and, thus, corresponds to neither the step period of 75 meV nor the typical phonon modes of hexagonal GaN.[18] Moreover, the strong intensity of the 2.731-eV line makes it an unlikely candidate for the ZPL of the steplike PLE structure. 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 $^6A_1(S)$-$^4E(G)$ transition. This assignment is supported by the weak phonon sideband typical for this transition.[26]

The spectral appearance of the steplike 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[27] or deeply bound electron-hole pairs.[28,29] The steps are located on the low-energy onset of the broad and efficient UV excitation band (Fig. 2, crystal 3) which we assign to the $Fe^{3+/2+}$ charge-transfer transition. We therefore attribute this structure to the formation of a shallow bound state at the Fe center.

Shallow bound states are now well established for the near-midgap acceptor Fe in III-V semiconductors.[30–32] The Coulomb interaction between the negatively charged Fe^{2+}

ion and a hole in the valence-band results in the formation of a (Fe^{2+},h) complex. In a first approximation the bound-hole state can be described by effective-mass theory and thus as a (transient) shallow-acceptor state. This complex is, in principle, an excited state of Fe^{3+} and relaxes nonradiatively to the excited $^4T_1(G)$ state. The exchange interaction between the loosely bound hole and the core holes influences the fine structure. In GaAs, GaP, and InP Fe forms a deep-acceptor level near the middle of the band gap with the core wave functions well localized at the Fe ion. The binding energy of the (Fe^{2+},h) complex amounts to only a few tens of a meV. As a consequence the overlap between the hole and the core wave functions is small and thus the exchange interaction is weak. This fact is demonstrated by the fivefold fine structure observed at the low-energy onset of the $Fe^{3+/2+}$ charge-transfer band in InP, GaP, and GaAs,[30–32] which reflects the Fe^{2+} term scheme. The exact location of the $Fe^{3+/2+}$ acceptor level in GaN is not clear yet. The observation of the charge-transfer band in PLE should provide this information. However, the superposition of shallow bound states of TM's to the low-energy slope of a charge-transfer band makes a fit of the ionization band impossible in order to determine the onset energy.[28,29] Nevertheless, it is reasonable to identify the energy (3.17±0.10 eV) at which the steplike structure vanishes and the broad structureless charge-transfer band begins to dominate with the energy position of the deep $Fe^{3+/2+}$ acceptor level. This assignment yields a binding energy of (280±100) meV for the shallow bound state of the Fe center in GaN.

Therefore, the deep $Fe^{3+/2+}$ acceptor level in GaN is close to the conduction-band minimum. This makes the hybridization of the core states important. Additionally, the binding energy of 280 meV of the shallow complex is much higher than in the other III-V semiconductors. Both effects add up to a strong exchange interaction. Therefore, a deeply bound electron-hole complex (Fe^{3+},e,h) is the appropriate description of this state. Nevertheless, the ionization products are still Fe^{2+} and a free hole. A very similar situation was demonstrated for shallow bound states of Ni comparing cubic ZnS and hexagonal CdS.[29] The strong phonon coupling causing the steplike structure as seen in Fig. 4 is typical for such a deeply bound electron-hole pair.[30] Recent calculations[33] show that the hybridization of the TM ground state with valence-band states is favored in hexagonal host crystals. Indeed, all known shallow states of TM's in wurzite crystals have the character of a (TM,e,h) complex.[28,29]

IV. DISCUSSION

The PLE spectra of the Fe^{3+} [$^4T_1(G)$-$^6A_1(S)$] luminescence in semi-insulating GaN samples (Fig. 2) allow us to deduce a comprehensive term scheme of the Fe^{3+} center in GaN (Fig. 5). Four crystal-field states of Fe^{3+} are identified. Their energy positions give a wealth of information for detailed ligand-field calculations which are beyond the scope of this paper. In principle, optical transitions of a d^5 configuration involving the $^6A_1(S)$ ground state have a low transition probability because of their spin-flip character. Only the luminescent $^4T_1(G)$ state exhibiting a ms lifetime is observed in narrow-band-gap III-V compounds such as InP, GaP, and GaAs. The higher excited states are expected to be degenerate with the conduction band. However, detailed information on higher excited states were derived by PLE investigations for Mn^{2+} in the wide-band-gap II-VI semiconductors.[19,26] From our results we conclude that the crystal-field splitting of the ^4G 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, the 3+ charge state of iron, and the high electronegativity of nitrogen. An increased crystal-field strength has been reported for other TM's in GaN, too.[11,12]

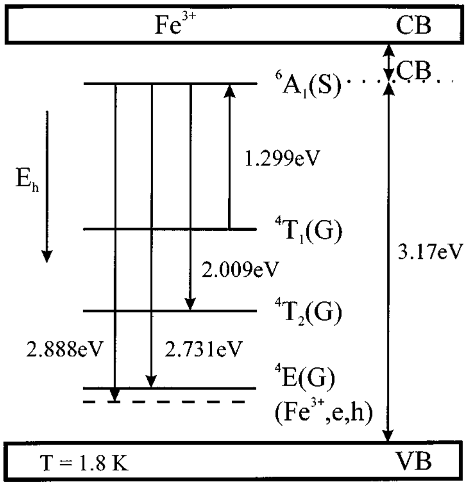

FIG. 5. Energy levels of the Fe^{3+} center in hexagonal GaN in the hole picture. The observed transition energies are given for a crystal temperature of $T=1.8$ K.

The possible excitation processes of the Fe^{3+} luminescence in the semi-insulating samples containing iron in the neutral 3+ charge state are obvious from the term scheme in Fig. 5. The sharp lines at 2.01- and 2.73-eV result from intracenter absorption into the excited crystal-field states and the (Fe^{3+},e,h) complex. The broad UV band is attributed to the acceptor-type charge-transfer process

$$Fe^{3+}(^6A_1(S))+h\nu\rightarrow Fe^{2+}+h_{VB}\rightarrow(Fe^{3+})^*. \qquad (1)$$

The recombination of holes with Fe^{2+} centers provides the most efficient excitation process of the Fe^{3+} luminescence in both III-V (Refs. 30–32) and II-VI (Refs. 23 and 24) semiconductors. For n-type GaN samples the direct excitation of Fe^{3+} is more complicated. Fe^{3+} has to be generated in an excited state starting from Fe^{2+} in a photoionization process:

$$Fe^{2+}(^5E)+h\nu\rightarrow(Fe^{3+})^*+e_{CB}. \qquad (2)$$

The probability of this transition is expected to be comparatively low due to s-d character of the electron transition. However, the low-energy thresholds for excitation into the $^4T_1(G)$ or $^4T_2(G)$ states are expected at 1.64 and 2.35 eV, respectively, whereas the experimental threshold is found at 2.2 eV, crystal 1 in Fig. 2. Thus, it is questionable if the observed PLE can be attributed to the $Fe^{2+/3+}$ charge-transfer excitation process [Eq. (2)]. The efficient visible excitation of the Fe^{3+} luminescence observed in n-type samples is more likely caused by the simultaneous presence of other defects in GaN acting as activator centers. In n-type

II-VI semiconductors excitation of the Fe^{3+} luminescence is provided by the capture of holes generated in charge-transfer processes of other TM defects.[23,24] Two-color stimulation experiments indicate that there is a similar excitation mechanism in n-type GaN with the deep defect of the yellow luminescence acting as a hole source.[34] Thus, the PLE spectra of the Fe^{3+} luminescence in n-type GaN yield information on other defects rather than on the Fe center itself. The PLE spectrum of crystal 2 represents a superposition of the PLE spectra observed in the n-type sample 1 and semi-insulating sample 3 showing that the Fermi level is pinned at the Fe level and that both, Fe^{3+} and Fe^{2+} are present in the unexcited crystal.

The PLE spectra presented in this paper differ considerably from those reported by Baur *et al.*[7,8] We assume that the better defined detection window enabled us to separate different luminescence processes and, thus, to obtain more reliable data. The ionization energy of 3.17 eV determined in this work is considerably higher than the value of 2.5 eV by Baur *et al.*[7,8] It should be noted that our observation of the formation of the (Fe^{3+},e,h) complex on the low-energy onset of the $\mathrm{Fe}^{3+/2+}$ charge-transfer band does not allow for much uncertainty in the deep-acceptor-level position.

The energy level of the acceptor close to the conduction band allows us to understand an otherwise very puzzling fact. Up to now it was not possible to detect the Fe^{2+} $({}^5E\text{-}{}^5T_2)$ transition in absorption or luminescence in n-type or semi-insulating samples even though it is very prominent in other semiconductors. The lack of luminescence may be the result of efficient nonradiative relaxation processes resulting from the large phonon energies.[35,36] Taking into account the position of the $\mathrm{Fe}^{3+/2+}$ level only 340 meV below the conduction band of GaN, it is now very likely that the excited ${}^5T_2$ state of Fe^{2+} is degenerate with the conduction band, explaining the absence of the intracenter transitions of Fe^{2+} in optical spectra.

The position of the $\mathrm{Fe}^{3+/2+}$ acceptor level has also a remarkable consequences for the interpretation of the other TM luminescence bands in GaN. The relative positions of the different TM charge-transfer levels in each component are usually out of question. These positions are well known for GaAs, GaP, and InP. In these semiconductors, the Ti and V acceptor levels are closer to the conduction band than that of Fe. With the $\mathrm{Fe}^{3+/2+}$ acceptor level 340 meV below the conduction band the Ti and V acceptor level would be degenerate with the conduction band in GaN. This gives different information regarding the interpretation of the chemical origin of the 1.19-eV luminescence, which was previously attributed to Cr^{4+} (Ref. 5) and to Ti^{2+}.[12] Also more detailed investigations are necessary to clarify the chemical origin of the 0.931-eV luminescence which was assigned to V^{3+}.[37]

The energies of deep levels of TM's are used to determine band offsets of semiconductor heterostructures[15,16] based on the internal reference rule for these defects. Even though the internal reference rule has been validated for many semiconductor TM combinations it is not clear if it can be used unambiguously to predict band offsets. Following the internal reference rule,[15,16] the position of the $\mathrm{Fe}^{3+/2+}$ acceptor level yields a type-II band alignment for the GaAs/GaN heterojunction with valence- and conduction-band offsets of 2.63 and 0.65 eV, respectively. These offsets are in disagreement with previous results of electrical measurements. These favored a type-I configuration with significant offsets in both the valence and conduction band.[38,39] Obviously, the internal reference rule does not hold for GaN in conjunction with GaAs, GaP, and InP. The reason may be the large difference between the electronegativity of nitrogen (3.00) on one side and that of phosphorus (1.64) as well as arsenic (1.57) on the other.[40] This argument can be supported considering ZnO which is comparable to GaN with respect to electronic and lattice properties. Like nitrogen among the group-V elements, oxygen has a much higher electronegativity than the other group-VI elements. With these similarities in mind it is interesting to note that for ZnO the internal reference rule does not hold with respect to the other II-VI semiconductors. Both the $\mathrm{Cu}^{2+/+}$ (Ref. 41) and the $\mathrm{Fe}^{3+/2+}$ (Ref. 24) levels are found directly below the conduction-band minimum which is not consistent with the internal reference rule. The theories presently available do not account for these deviations. Among the nitrides the internal reference rule is assumed to give reasonable values for band offsets. With a valence-band offset of 0.8 eV for GaN/AlN (Refs. 42, 43) the $\mathrm{Fe}^{3+/2+}$ acceptor level is expected to be 4 eV above the valence band of AlN. This energy is much larger than the charge-transfer energy of 2.97 eV derived from PLE spectra.[7,8] However, Refs. 7 and 8 neither give arguments for Fe to be stable in the 3+ charge state nor present fine structures in the charge-transfer band. It is possible that the PLE spectrum presented in Refs. 7 and 8 correspond to the n-type case and, thus, does not yield information on the $\mathrm{Fe}^{3+/2+}$ level.

V. SUMMARY

In this paper we presented detailed photoluminescence excitation results for the Fe^{3+} $[{}^4T_1(G)\text{-}{}^6A_1(S)]$ luminescence in hexagonal GaN. Two crystal-field transitions, ${}^6A_1(S)\text{-}{}^4T_2(G)$ and ${}^6A_1(S)\text{-}{}^4E(G)$ were resolved with ZPL's at 2.01 and 2.731 eV, respectively. Additionally, a deeply bound electron-hole complex (Fe^{3+},e,h) with a binding energy of (280 ± 100) meV was observed. A strong phonon coupling leads to a steplike structure in PLE on the low-energy side of the $\mathrm{Fe}^{3+/2+}$ charge-transfer band. The $\mathrm{Fe}^{3+/2+}$ acceptor level is located 0.34 eV below the conduction-band minimum which has important implications for the use of the $\mathrm{Fe}^{3+/2+}$ level to determine band offsets. The internal reference rule was found not to be applicable to the GaN/GaAs heterostructure, a fact that we attribute to the high electronegativity of nitrogen.

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