PHYSICAL REVIEW B VOLUME 52, NUMBER 23 15 DECEMBER 1995-I

# Identification of the 1.19-eV luminescence in hexagonal GaN

R. Heitz, P. Thurian, I. Loa, L. Eckey, A. Hoffmann, and I. Broser
*Institut für Festkörperphysik, Technische Universität Berlin, 10623 Berlin, Germany*

K. Pressel
*Institut für Halbleiterphysik, 15204 Frankfurt/Oder, Germany*

B. K. Meyer
*Physik-Department E16, Technische Universität München, 85748 Garching, Germany*

E. N. Mokhov
*Joffe Physico-Technical Institute, 1904021 St. Petersburg, Russia*
(Received 27 June 1995)

We report on optical investigations of a near-infrared luminescence band in hexagonal GaN with a single zero-phonon line (ZPL) at 1.1934 eV. It is attributed to the spin-forbidden internal $d$-$d$ transition $^1E(D)$-$^3A_2(F)$ of a defect with a $d^2$ electronic configuration. This assignment is based on the observed Zeeman splittings, which agree with the ground and excited states being threefold and twofold degenerate, respectively. This interpretation is supported by the observed small full width at half maximum (FWHM) of the ZPL, the weak phonon sideband, and the weak temperature dependence of the luminescence band. With increasing temperature, the ZPL shifts towards lower energies but maintains its FWHM of about 200 $\mu$eV up to 60 K. The observed luminescence lifetime of 65 $\mu$s indicates a strong mixing of the $^1E(D)$ with the $^3T_2(F)$ multiplet at slightly higher energies by spin-orbit interaction. Photoluminescence excitation spectra show intracenter absorption into the higher excited $^3T_1$ states at 1.62 and 2.8 eV in $n$-type samples, proving the defect to be in the luminescent charge state in $n$-type material. Thus, we propose $Ti^{2+}$ as the luminescence center responsible for the 1.19-eV transition. Implications for the band offset between GaN and GaAs are discussed.

## I. INTRODUCTION

Nitrides have gained increasing interest in the past few years, due to their potential for optoelectronic devices operating in the blue spectral region.[1] In particular, the interest in GaN results from the considerable improvements of growth techniques and advances in device applications, e.g., the possibility of $p$ doping,[2] and the commercial availability of efficient blue light-emitting diodes.[3] However, no electrically pumped nitride-based lasers have been demonstrated yet. The main drawback of the nitrides is the lack of a lattice-matched substrate material for epitaxial growth. Bulk GaN can be grown at extremely high pressure[4] but it is still not commercially available. Transition metals remain the omnipresent contaminations in GaN influencing the electrical and optical properties. They comprise a considerable technological potential, e.g., for the generation of semi-insulating material. Additionally, deep transition-metal levels yield estimates for band offsets.[5,6] Nevertheless, transition metals in general open efficient relaxation channels, thus degrading the near-band-gap luminescence efficiency[7] and hampering device performance. So far, very little information on transition-metal centers and especially their optical properties exists.

Recently, various structured near-infrared luminescence bands have been reported for GaN.[8,9] However, only one of these bands has been unambiguously identified. Optically detected magnetic resonance (Ref. 10) as well as Zeeman[11] spectra reported for the 1.3-eV band show the clear fingerprint of a $^6A_1(S)$ ground state of a $d^5$ electronic configuration. The luminescence is attributed to the spin-forbidden internal $d$-$d$ transition $^4T_1(G)$-$^6A_1(S)$ of $Fe^{3+}$ on Ga sites. Moreover, excitation measurements of the $Fe^{3+}$ luminescence in GaN and AlN have been exploited to estimate band offsets from the position of the deep $Fe^{2+/3+}$ acceptor level.[6,12] The identification of further structured luminescence bands with zero-phonon lines (ZPL's) at 1.193, 1.047, and 0.931 eV is rather tentative. All three luminescence bands have been attributed to the symmetry-forbidden $^3T_2(F)$-$^3A_2(F)$ transition of an electronic $d^2$ configuration with either $V^{3+}$ or $Cr^{4+}$ as defect.[8,9,13]

In this paper we report on optical and magneto-optical measurements leading to a detailed characterization of the electronic and chemical origin of the 1.19-eV band in hexagonal GaN samples grown on 6H-SiC substrates. We deduce that the electron-phonon coupling in both the

0163-1829/95/52(23)/16508(8)/$06.00  ©1995 The American Physical Society

excited and the ground state of the luminescence is weak from the observation of the weak phonon sideband as well as the weak temperature dependence of the 1.19-eV band, which are quite unusual for an internal transition of a 3*d* transition-metal center. The results of Zeeman spectroscopy, however, give clear evidence for an electronic $d^2$ configuration of a transition metal. Here we demonstrate unambiguously that the 1.19-eV luminescence in GaN results from the spin- and symmetry-forbidden ${}^1E(D)$-${}^3A_2(F)$ transition. Excitation spectra show efficient excitation via the spin- and symmetry-allowed intracenter ${}^3A_2(F)$-${}^3T_1$ absorption bands in *n*-type material proving the stability of the defect in the luminescent charge state in *n*-type material in the dark. We attribute the 1.19-eV luminescence band to the ${}^1E(D)$-${}^3A_2(F)$ transition of $Ti^{2+}$ on Ga sites.

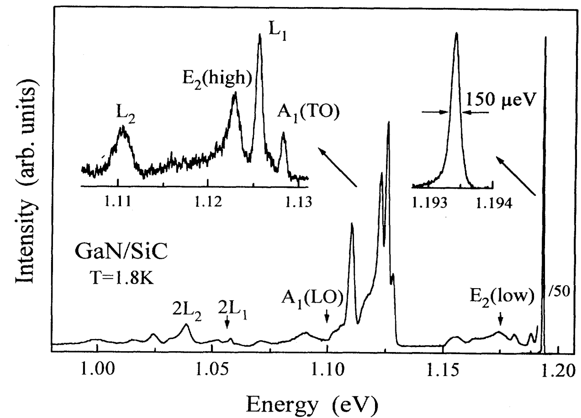


FIG. 1. Luminescence spectrum of the 1.19-eV emission in *n*-type GaN excited at 1.83 eV ($T=1.8$ K). The insets show on enlarged energy scales the ZPL at 1.1934 eV and the region of pronounced optical phonon replicas.

## II. EXPERIMENT

The hexagonal GaN epilayers investigated in this paper are grown on 6H-SiC substrates using a modification of the sublimation sandwich method described earlier.[14] The samples are *n* type,[9] with free carrier concentrations above $10^{17}$ cm$^{-3}$. The appearance of the 1.3-eV photoluminescence indicates a general contamination of these samples with Fe.[9,11] A chemical analysis of the epilayers reveals, in addition to Fe, also Cr, Ti, and Ni as unintentional dopants.

Luminescence was excited by either the 488-nm line of an $Ar^+$ laser, the 676-nm line of a Kr laser, or a dye laser tuned at 680 nm. The emission of the sample was then dispersed by a 0.75-m double-grated monochromator and detected with a cooled slow Ge photodiode (North Coast 817L). Temperature-dependent measurements were performed using a BOMEM DA8.02 Fourier-transform infrared spectrometer. For time-resolved experiments we used a cooled fast Ge photodiode (North Coast 817P) and a boxcar integrator giving a time resolution better than 4 $\mu$s. Magnetic fields up to 15 T were provided by a superconducting magnet built in split-coil configuration. The Zeeman experiments are performed in Voigt configuration at sample temperatures between 2 and 10 K. Luminescence excitation spectra were recorded with a tungsten lamp dispersed by a 0.35-m double-grated monochromator as tunable light source and a double prism monochromator as tunable spectral filter for the luminescence.

## III. RESULTS

GaN samples grown by the sublimation sandwich technique show at least three clearly distinguishable structured luminescence bands in the near-infrared spectral region with ZPL's at 1.3, 1.19, and 1.047 eV.[9] The 1.3- and 1.19-eV bands occur in metal-organic chemical-vapor deposition grown samples, too, indicating omnipresent defects. Here, we present a thorough investigation of the 1.19-eV band shown in detail in Fig. 1. The luminescence band shows a single sharp ZPL at 1.1934 eV, with a full width at half maximum (FWHM) of only 150 $\mu$eV (inset Fig. 1). The FWHM of this ZPL varies slightly with the sample investigated or the position on the sample but is always significantly smaller than that of the ZPL's of the ${}^4T_1(G)$-${}^6A_1(S)$ transition of $Fe^{3+}$ (800 $\mu$eV) and of the 1.047-eV luminescence (2.1 meV). The near-band-gap luminescence of the sample shown is dominated by the recombination of donor-bound excitons with a FWHM of 4 meV. The phonon sideband of the 1.19-eV luminescence is unusually weak for an internal *d*-*d* transition of a 3*d* impurity in III-V compounds. The strongest phonon replica has about 2% of the intensity of the ZPL. Magnified spectra reveal a weak coupling to acoustical phonons with a pronounced structure near $E_2$ (low) ($\approx 18$ meV) and some sharp phonon replicas in the region of optical phonons of the hexagonal GaN host crystal. The phonon replicas with energies of 65.1 and 70.5 meV almost coincide in energy with the $A_1$(TO) and the $E_2$ (high) observed in Raman spectra.[15] The occurrence of typical Raman modes of hexagonal GaN in the phonon sideband proves the hexagonal coordination of the luminescence center. Two well-defined replicas $L_1$ and $L_2$, corresponding to phonon energies of 67.8 and 82.2 meV, are assigned to local modes of the defect center. The weak phonon sideband and the observation of sharp host phonon replicas indicate that the electron-phonon coupling is weak in both the excited and the ground state of the 1.19-eV luminescence.

Figure 2 depicts the photoluminescence transient observed for the ZPL at 1.1934 eV after excitation at 680 nm. The luminescence decays exponentially with a time constant $\tau_0$ of $65\pm15$ $\mu$s. This lifetime is typical for a symmetry-forbidden *d*-*d* transition.[16]

Figure 3 shows the zero-phonon region of the 1.19-eV band for various sample temperatures. The sample is excited at 514 nm. The 1.19-eV luminescence band is only weakly affected by temperatures up to 50 K. At higher temperatures the luminescence intensity drops and the ZPL shifts towards lower energies and becomes broader.

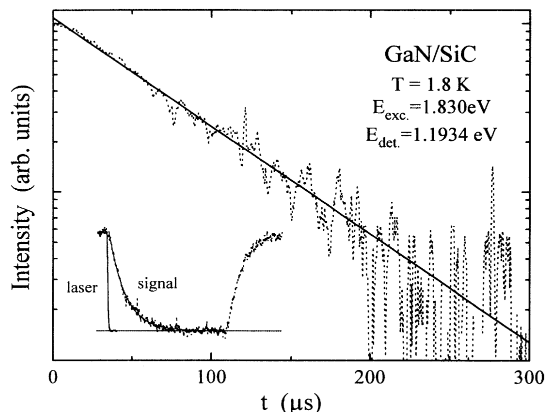


FIG. 2. Luminescence transient of the 1.19-eV emission at $T=1.8$ K. The luminescence is excited with modulated light at 1.83 eV and detected on the ZPL at 1.1934 eV. The full line represents a single exponential fit.

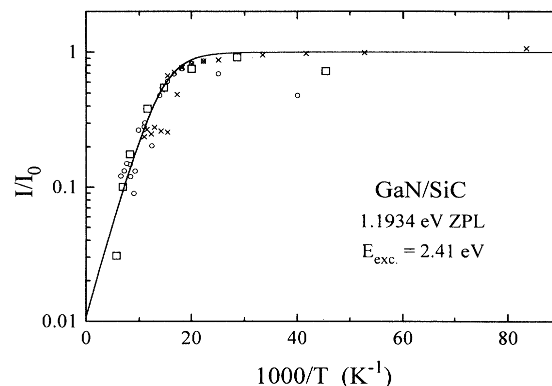


FIG. 4. Temperature dependence of the integral intensity of the 1.1934-eV ZPL in GaN. The full line represents a fit with Eq. (1). (The results of three different temperature series are depicted.)

It has to be emphasized that no hot line evolves on the high-energy side of the ZPL, indicating the lack of further fine-structure components. Very recently, a hot line has been claimed at the position marked by the dotted line in Fig. 3.[13] This line is completely missing in all our spectra of the 1.1934-eV ZPL.

For the evaluation of the temperature dependence of the intensity, lineshift, and full width at half maximum of the 1.1934-eV ZPL, the data of three different temperature series are compiled. The samples are inhomogeneous and, thus, small changes of the optical alignment can obscure the results. Figure 4 depicts the temperature dependence of the integral intensity of the ZPL, which decreases above 50 K. The ZPL is resolved up to 175 K. The temperature-dependent intensity can be described assuming an exponential activation of competing nonradiative processes

$$\frac{I}{I_0}=\left[1+\frac{\tau_0}{\tau_{\mathrm{nr}}}\exp\left[-\frac{E_A}{kT}\right]\right]^{-1} . \tag{1}$$

$\tau_0$ is the radiative lifetime and $E_A$ is the activation of the competing nonradiative relaxation process of probability $\tau_{\mathrm{nr}}^{-1}$. The solid line in Fig. 4 represents a fit with Eq. (1) giving a nonradiative decay time $\tau_{\mathrm{nr}}$ of 720 ns and an activation energy $E_A$ of 28 meV.

Figure 5(a) depicts the temperature-dependent energy shift $\Delta E$ of the ZPL with respect to the low-temperature

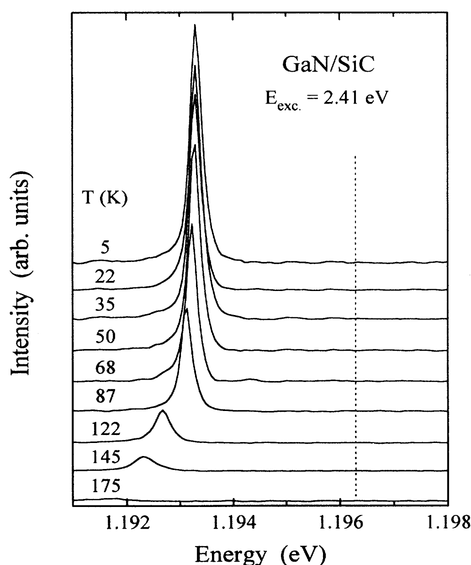


FIG. 3. The ZPL region of the 1.19-eV emission in GaN for various sample temperatures. The position of the hot line claimed in Ref. 13 is indicated by the dotted line. The hot line does not appear in our samples.

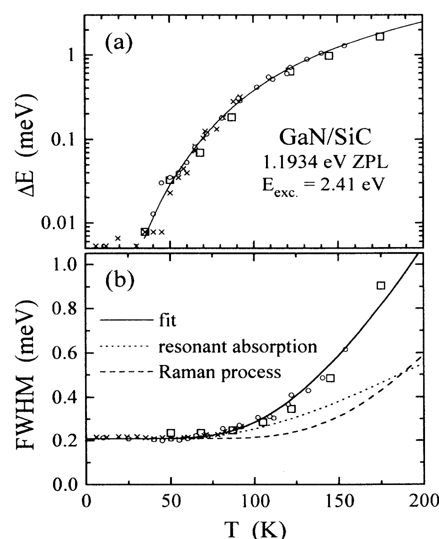


FIG. 5. Temperature dependence of (a) the energy shift ($\Delta E$) and (b) the linewidth (FWHM) of the 1.1934-eV ZPL in GaN. Lines represent fits with Eqs. (2) and (3), respectively. (The results of three different temperature series are depicted.)

position in a semilogarithmic plot. The shift reaches 1.7 meV at 175 K. Such temperature shifts of sharp *d-d* transitions of 3*d* elements in crystals are well known.[17] In semiconductors, however, strong line broadening at low temperatures often prevents the resolution of these shifts. It has been demonstrated that the energy shift of a fine-structure transition results from phononic Raman processes in both the excited and ground states of the optical transition and can be described by[17]

$$\Delta E = \alpha \left[ \frac{T}{T_D} \right]^4 \int_0^{T/T_D} \frac{x^3}{e^x - 1} dx \ , \tag{2}$$

with $\alpha$ a measure for the scattering probability and $T_D$ the Debye temperature. Equation (2) gives an excellent fit of the experimental data [see full line in Fig. 5(a)] yielding 65 meV and 550 K for $\alpha$ and $T_D$, respectively. A Debye temperature of 600 K has been estimated from the refraction index in hexagonal GaN.[18] The Raman process contributes to the temperature dependence of the FWHM of the ZPL as well. Additionally, resonant phonon absorption and emission processes between different fine-structure components in the ground and/or excited state contribute to the FWHM,[17]

$$\mathrm{FWHM} = W_0 \coth \left[ \frac{\hbar\omega}{2kT} \right] + \beta \left[ \frac{T}{T_D} \right]^7 \int_0^{T/T_D} \frac{x^6 e^x}{(e^x - 1)^2} dx \ . \tag{3}$$

The first term on the right-hand side of Eq. (3) describes a resonant phonon process with $W_0$ as a measure for the spontaneous transition probability and $\hbar\omega$ the resonant phonon energy. The second summand gives the contribution of the Raman process to the line broadening with $\beta$ the coupling constant. Figure 5(b) depicts the temperature development of the FWHM of the ZPL. The low-temperature FWHM of 210 $\mu$eV results from inhomogeneous broadening. Depending on the sample and the sample position we observed FWHM's down to 150 $\mu$eV; see Fig. 1. At temperatures above 60 K, line broadening is observed and the FWHM reaches 1 meV at approximately 175 K. The full line in Fig. 5(b) represents a fit with Eq. (3). The dominating contribution at higher temperatures results from the Raman process ($T_D = 550$ K, $\beta = 32$ meV). At intermediate temperatures, a one-phonon process with 0.39 and 16 meV for $W_0$ and $\hbar\omega$, respectively, seems to be important. The presented experimental data, however, are not sufficient for a definite fit. In most cases, the temperature dependence of the FWHM of transition-metal ZPL's in semiconductors is dominated by resonant one-phonon transitions between fine-structure components in the ground and/or excited state. Thus, the temperature behavior of the 1.1934-eV ZPL strongly indicates the absence of any fine-structure splitting in the order of up to some meV in the ground and excited states of the 1.19-eV emission.

Figure 6 shows a typical excitation spectrum of the 1.19-eV luminescence in *n*-type GaN recorded at an excitation density below 20 mW cm$^{-2}$. The excitation spectrum is dominated by a band around 1.7 eV. The absorption starts at 1.62 eV and shows a triplet structure. The luminescence spectrum shown in Fig. 1 is excited at 1.83 eV showing the 1.19-eV emission virtually background-free. The shape of the 1.7-eV band is rather typical for an intracenter transition and is thus attributed to absorption ending in a higher excited multiplet. A further excitation band exists around 2.8 eV, which could be either a charge transfer or a further intracenter transition. The observation of resonant excitation via absorption inverse to the 1.19-eV luminescence transition was prevented by stray light. The excitation efficiency in the blue/green spectral region is at least a factor of 10 smaller than in the 1.7-eV band. When excited in the blue/green spectral region with an Ar laser, the ZPL of the 1.19-eV band is observed with a broad luminescence background originated from the $Fe^{3+}$ $[^4T_1(G)$-$^6A_1(S)]$ transition.[9]

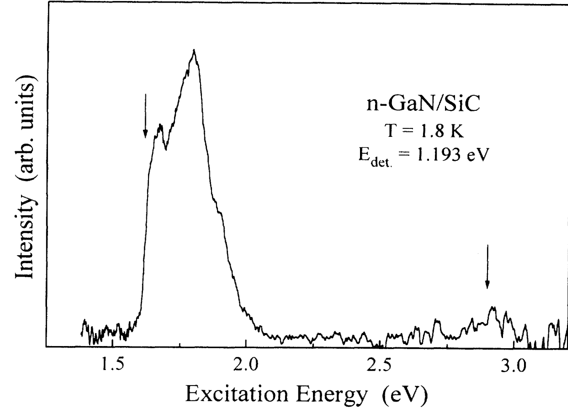


FIG. 6. Excitation spectrum of the 1.19-eV emission in *n*-type GaN ($n \geq 10^{17}$ cm$^{-3}$) at $T = 1.8$ K. The luminescence is detected at 1.1934 eV. The arrows indicate excitation bands corresponding to transitions into higher excited $^3T_1$ states at 1.62 and 2.8 eV.

In order to identify the electronic structure of the luminescence center, we have investigated the Zeeman behavior of the ZPL at 1.1934 eV. Figure 7 shows the spectral region of the ZPL in magnetic fields oriented either parallel ($B \| c$) or perpendicular ($B \perp C$) to the *c* axis of the hexagonal GaN sample. In the Zeeman experiments, the spectral resolution was limited by the experimental setup to 250 $\mu$eV. For $B \perp c$ the ZPL splits into a symmetrical triplet. For $B \| c$ each component of the triplet splits additionally into a doublet. Measurements at higher temperatures show no intensity variation for the components of the triplet, which indicates that these components represent the splitting of the ground state of the luminescence. On the contrary, the high-energy component of the doublets resolved for $B \| c$ gains intensity with increasing temperature, ascribing this splitting to the excited state. Figure 8 compiles the Zeeman components of the 1.1934-eV ZPL in dependence on the magnetic field strength. The open squares correspond to lines dominating at 2 K and open circles represent those gain-

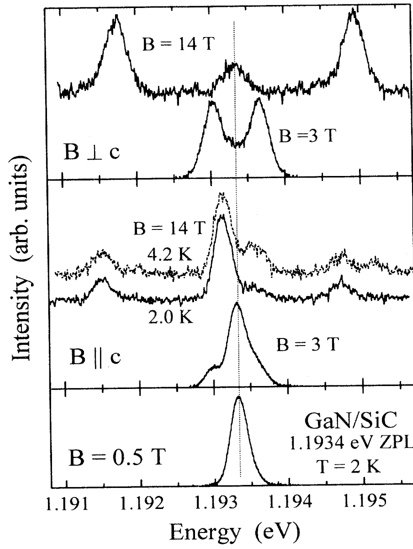


FIG. 7. Zeeman splitting of the 1.1934-eV ZPL with the magnetic field orientated either parallel ($B\|c$) or perpendicular ($B\perp c$) to the $c$ axis of the hexagonal GaN. The spectral resolution is limited by the experimental setup.

ing intensity at higher temperatures. Full and dashed lines in Fig. 8 represent a fit of the experimental data using

$$\Delta E = g_{\rm gr}\mu_B B m_J^{\rm gr} + g_{\rm exc}\mu_B B m_J^{\rm exc} , \quad (4)$$

with $g_{\rm gr}$ and $g_{\rm exc}$ the $g$ values of the excited and the ground state, respectively, $\mu_B$ the Bohr's magneton, and we assume a triplet for the ground state and a doublet for the excited state. The ground-state $g$ value is found to be isotropic with $1.98\pm0.03$, whereas the $g$ value of the excited state is anisotropic. The doublet splitting observed for $B\|c$ corresponds to a $g$ value of $0.51\pm0.05$, whereas

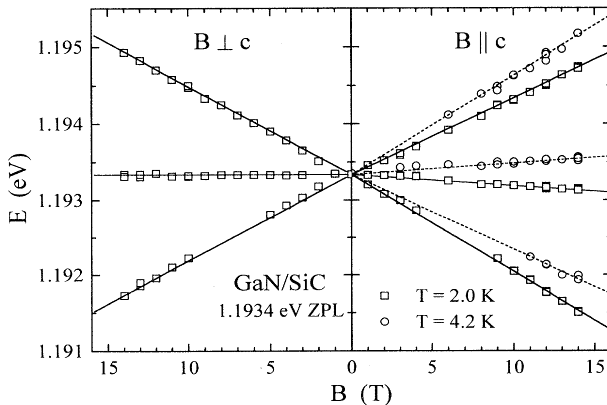


FIG. 8. Observed Zeeman splitting (open squares and circles) of the 1.1934-eV ZPL with the magnetic field orientated either parallel ($B\|c$) or perpendicular ($B\perp c$) to the $c$ axis of the hexagonal GaN. Full and dashed lines represent a fit with Eq. (4).

for $B\perp c$ no splitting could be resolved, giving an upper limit of 0.15. In principle, the trigonal crystal field in hexagonal GaN should result at least in a zero-field splitting of the triplet ground state. We are not able to resolve the zero-field splitting, hence yielding an upper limit of 40 $\mu$eV. It has to be noted that the Zeeman splitting of the 1.1934-eV ZPL (Fig. 8) is totally symmetric with respect to the zero-field position. In general, term interactions with nearby fine-structure components lead to a superimposed nonlinear shift towards lower energies for the fine-structure transition lowest in energy. Thus, the Zeeman experiments show, in agreement with the temperature-dependent data, the absence of such states for the 1.19-eV emission.

## IV. DISCUSSION

The electronic and chemical origin of the 1.19-eV emission in GaN, which is obviously connected with an omnipresent contaminant, is unclear. Recently, it has been attributed to the symmetry-forbidden $^3T_2(F)$-$^3A_2(F)$ transition of $Cr^{4+}$.[8,13] The major argument is associated with the observation of a hot line 3.1 meV above the ZPL, which is claimed but not shown in Ref. 13. Such a splitting would be rather typical for a $^3T_2(F)$ state of an electronic $d^2$ configuration. In our samples, however, we do not observe this hot line (Fig. 3). On the contrary, our results of both Zeeman and temperature-dependent measurements of the 1.1934-eV ZPL show the absence of such a state, which makes the assignment of the 1.19-eV emission to the $^3T_2(F)$-$^3A_2(F)$ transition of $Cr^{4+}$ doubtful.

Our results allow us some general remarks about the luminescence center. First of all, it has to be an isolated point defect. Although we were not able to resolve polarization of the optical transitions expected in a hexagonal host, the anisotropic Zeeman splitting of the excited state (Fig. 8) with respect to the $c$ axis of the hexagonal GaN crystal evidences a point defect. The shape of the phonon sideband and the temperature behavior of the ZPL of the 1.19-eV luminescence are rather typical for rare-earth (RE) defects. However, unintentional contamination with RE elements is unlikely and those RE centers having nearly matching transition energies should show fine structure in the ground state, which is not observed in our experiments. Additionally, it would be difficult to explain the intracenter excitation bands showing a strong phonon coupling. The 4$d$ and 5$d$ transition metals are also unlikely contaminants and, additionally, the large mass difference to the replaced Ga atom would result in local modes dominating the phonon sideband in luminescence,[19] which is not the case for the 1.19-eV emission in GaN.

The Zeeman results yield detailed information about the electronic origin of the 1.19-eV luminescence band. The ground state is obviously a spin triplet ($S=1$) with an isotropic $g$ value of 1.98 and a trigonal zero-field splitting of less than 40 $\mu$eV. Only the electronic $d^2$ configuration offers an adequate ground-state multiplet with the $^3A_2(F)$ state. The identification of the excited state is much more difficult. Depending on the cubic

crystal-field strength, either the triplet $^3T_2(F)$ or the singlet $^1E(D)$ will be the first excited state[20] (see schematic Tanabe-Sugano diagram in Fig. 9), and, thus, should be observed in luminescence. For $3d$ defects in semiconductors with a $d^2$ configuration, the $^3T_2(F)$ state has been identified as the first excited state.[21–24] It is characterized by a doublet structure with a splitting of a few meV. A strong dynamical Jahn-Teller coupling to ε-type modes quenches the first-order spin-orbit coupling, leading to a doublet splitting by second-order interactions.[25] For $V^{3+}$ in the cubic semiconductors InP, GaAs, and GaP, the splitting amounts to 1.53, 1.27, and 1.93 meV, respectively.[22–25] This doublet structure is missing in the case of the excited state of the 1.19-eV emission in GaN. The hexagonal crystal structure of GaN will alter the fine structure of the $^3T_2(F)$ multiplet due to the additional trigonal crystal field and a stabilization of the center against Jahn-Teller distortions.[11] A comparison with the quite similar hexagonal semiconductor ZnO shows, however, that only additional fine structure can be expected.[26] The $^3T_2(F)$ multiplet shows a characteristic Zeeman behavior in cubic III-V semiconductors.[22–25] The lower fine-structure state shows an anisotropic doublet splitting which quenches for $B\|[111]$. This orientation corresponds to $B\|c$ in hexagonal GaN. In principle, this is consistent with our experimental results (Fig. 8), but term interaction with the excited state of the hot line causes a clearly resolvable nonlinear low-energy shift of the components of the low-temperature line, which is not observed for the 1.1934-eV ZPL in GaN. Additionally, the $C_{3V}$ crystal field is found to strongly alter the Zeeman behavior. In ZnO an almost isotropic $g$ value of 1.78 is observed for the low-temperature line,[26] which drastically differs from our results.

From the above discussion, it has to be concluded that in GaN the singlet $^1E(D)$ state is shifted below the triplet $^3T_2(F)$ state as indicated in Fig. 9. A similar experimental situation has been reported for the $4d$ transition metal Nb in GaAs.[27] The 0.7956-eV ZPL in GaAs shows a totally symmetric threefold splitting in a magnetic field,

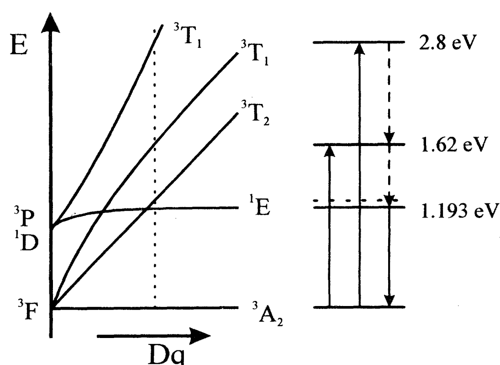


FIG. 9. Schematic Tanabe-Sugano diagram with the dotted line giving the proposed crystal-field strength for $Ti^{2+}$ in GaN. The observed optical transitions are indicated by arrows in the term scheme on the right-hand side.

similar to that observed here for the 1.1934-eV ZPL in GaN. The luminescence has been attributed to the $^1A$-$^3A_2(F)$ transition of the $d^2$ configuration of $Nb^{2+}$. This identification may be reinterpreted taking into account the $^1E(D)$ multiplet as excited state in view of the experimental results presented here for the 1.19-eV emission in GaN.

The $^1E(D)$-$^3A_2(F)$ transition explains most of the experimental fine-structure data of the 1.19-eV emission in GaN. Considering spin-orbit interaction, the ZPL corresponds to the dipole-allowed $\Gamma_3$-$\Gamma_5$ transition. The trigonal crystal field splits the threefold-degenerate $\Gamma_5$ ground state into a $\Gamma_1$ singlet and a $\Gamma_3$ doublet, leading to two polarized ZPL's. The 1.1934-eV ZPL, however, is too broad to allow us to resolve the doublet splitting and shows no clear polarization behavior. For both the $^1E(D)$ and the $^3A_2(F)$ multiplet, any Jahn-Teller interaction is expected to be weak. This explains the weak phonon sideband in luminescence, which shows mainly replicas due to modes of the hexagonal GaN host crystal. The lack of any fine-structure splitting in both multiplets accounts for the totally symmetric Zeeman behavior and the weak temperature dependence. It is interesting to note that the temperature behavior of the 1.1934-eV ZPL is quite similar to that of the $^2E(D)$-$^4A_2(F)$ transition of, e.g., $V^{2+}$ in MgO,[28] described by 49.6 and 46.8 meV for $\alpha$ and $\beta$, respectively. In a Tanabe-Sugano diagram,[20] the $^1E(D)$ multiplet shifts almost parallel to the $^3A_2(F)$ ground state. Thus, a variation of the cubic crystal field due to internal strain in the samples has little influence on the transition energy. Indeed, the FWHM of the 1.1934-eV ZPL is much smaller than that of the ZPL's of the 1.3- and 1.047-eV emissions in the investigated samples.

The luminescence decay time of 65 $\mu$s is, however, unexpectedly short for a spin- and symmetry-forbidden transition[11,16] like the $^1E(D)$-$^3A_2(F)$ transition. It is rather typical for the spin-allowed $^3T_2(F)$-$^3A_2(F)$ transition.[29] Competing nonradiative relaxation processes, which generally cannot be neglected for internal transitions of $3d$ elements,[30] shorten the lifetime of the exciting state but simultaneously decrease the quantum efficiency of the luminescence transition. However, for the 1.19-eV emission the electron-phonon coupling is weak in both the excited and ground states and the luminescence is comparatively intensive, making competing nonradiative processes unlikely. The short lifetime is rather the result of strong mixing with the triplet $^3T_2(F)$ multiplet situated at slightly higher energies by spin-orbit interaction. Obviously, the 1.19-eV center is close to the crossing point of the $^3T_2(F)$ and the $^1E(D)$ multiplet in the Tanabe-Sugano diagram, Fig. 9.

The 1.7-eV absorption band observed in excitation spectra of the 1.19-eV emission (Fig. 6) is characteristic for the $d^2$ configuration. Absorption spectra of V-doped ($3d^2$) III-V semiconductors[31] always show more or less the same triplet structure as observed here in GaN. It is attributed to the spin- and symmetry-allowed transition from the $^3A_2(F)$ ground to the first excited $^3T_1$ state as indicated in Fig. 9. The structure of the absorption band is the result of a dynamical Jahn-Teller coupling in the

$^3T_1$ state.[32] The weak excitation band centered at 2.8 eV might be attributed to the transition into the second $^3T_1$ state. The proposed energy scheme of the 1.19-eV luminescence center is given on the right-hand side of Fig. 9.

A straightforward chemical identification of the luminescence center of the 1.19-eV band is not possible yet. Among the $3d$ transition metals, only three candidates offer an electronic $d^2$ configuration in III-V semiconductors: $Ti^{2+}$, $V^{3+}$, and $Cr^{4+}$. A chemical analysis of our samples shows that all three are unintentional dopants. However, the observation of efficient excitation of the $^1E(D)$-$^3A_2(F)$ luminescence via the intracenter $^3A_2(F)$-$^3T_1$ absorption bands in $n$-type samples (Fig. 6) demonstrates the presence of the luminescence center in its active charge state in $n$-type material. Otherwise, an efficient charge-transfer process of the luminescence center has to take place prior to excitation, leading to a two-step excitation mechanism. Such a process is rather unlikely at excitation densities below 20 mW $cm^{-2}$ used in our excitation measurements (see Fig. 6). The energy positions of deep levels introduced by transition metals in GaN can be estimated using the internal reference rule.[5] Across a heterointerface the energy position of a deep transition-metal level remains constant. Thus, knowing one energy level in two semiconductors yields band offsets or vice versa. However, the band offset between GaN and, e.g., GaAs is still controversially. Conduction-band offsets between 0 and 0.9 eV have been proposed.[6,12,33] For this span of band offsets the internal reference rule predicts Cr, V, and Ti to be in the 2+ charge state in $n$-type GaN. Thus, we propose isolated $Ti^{2+}$ on Ga sites as the luminescence center, since Ti is the only $3d$ transition-metal center expected to be stable in the $d^2$ configuration in $n$-type GaN.

The excited $^1E(D)$ state of $Ti^{2+}$ is still in the bandgap of GaN as demonstrated by the sharp ZPL of the 1.19-eV emission. The $Ti^{3+/2+}$ acceptor level in GaAs has been identified by deep-level transition spectroscopy to be 0.23-eV below the conduction band.[34] Thus, the conduction-band offset between GaN and GaAs has to be larger than 0.96 eV, which is in reasonable agreement with the value given in Ref. 33. The structure in the $^3A_2(F)$-$^3T_1$ absorption (Fig. 6) might indicate that the first excited $^3T_1$ state at 1.62 eV is still in the band gap. However, absorption and photoconductivity excitation spectra in $n$-GaAS:Ti show absorption bands due to transitions into the $^3T_1$ states although these are deep in the conduction band.[34,35] At least the second $^3T_1$ state in GaN at 2.8 eV will be in the conduction band, which could explain the lower excitation efficiency by autoionization.

## V. CONCLUSION

We have reported a detailed optical study of the 1.19-eV luminescence in as-grown hexagonal GaN. The luminescence is identified as the spin- and symmetry-forbidden $^1E(D)$-$^3A_2(F)$ transition of an electronic $d^2$ configuration. Taking into account the $n$-type character of the investigated samples and the internal reference rule, we conclude that $Ti^{2+}$ is the luminescence center.

The $^1E(D)$-$^3A_2(F)$ transition of $Ti^{2+}$ is in good agreement with all our experimental results. The phonon sideband of the luminescence is unusually weak. Most replicas are found to almost coincide in energy with Raman modes of hexagonal GaN. The Zeeman experiments show a totally symmetric behavior resulting from a threefold-degenerate ground-state splitting with $g=1.98$ and a twofold-degenerate excited state having an anisotropic $g$ value. The Zeeman behavior and temperature dependence of the ZPL at 1.1934 eV exclude any close lying fine-structure states in the ground and excited multiplets. Phonon-scattering processes hold for the small energy shift and the broadening of the ZPL with increasing temperature. A luminescence decay time of 65 $\mu$s is found and attributed to a strong mixing with the triplet $^3T_2(F)$ multiplet situated directly above the luminescent $^1E(D)$ state by spin-orbit coupling. The excitation spectra in $n$-type GaN are dominated by the spin- and symmetry-allowed intracenter absorptions into the $^3T_1$ states.

$Ti^{2+}$ is the first transition metal in GaN for which more than one excited state is known. Thus, basic parameters of transition-metal centers, e.g., Racah parameters and the cubic crystal-field strength, can be evaluated. The $^1E(D)$-$^3A_2(F)$ transition of $Ti^{2+}$ shows a noticeably higher cubic crystal-field strength in GaN compared to other III-V semiconductors. Any fit of the crystal-field states has to consider spin-orbit interaction to account for the pronounced mixing of the $^3T_2(F)$ and the $^1E(D)$ multiplet.

## ACKNOWLEDGMENT

Parts of this work have been supported by the Deutsche Forschungsgemeinschaft.


[1] S. Strite and H. Morkoc, J. Vac. Sci. Technol. B **10**, 1237 (1992).

[2] H. Amano, M. Kito, K. Hiramatsu, and I. Akasaki, Jpn. J. Appl. Phys. **28**, L2112 (1989).

[3] S. Nakamura, T. Mukai, and M. Senoh, Appl. Phys. Lett. **64**, 1687 (1994).

[4] S. Porowski, J. Jun, M. Bockowski, M. Leszczynski, St. Krukowski, M. Wroblewski, B. Lucznik, and I. Grzegory, in *Proceedings of the 8th Conference on Semi-insulating III-V Materials, Warsaw, Poland,* edited by M. Godlewski (World Scientific, Singapore, 1994), p. 61.

[5] J. M. Langer, C. Delerue, M. Lannoo, and H. Heinrich, Phys. Rev. B **38**, 7723 (1988).

[6] J. Baur, M. Kunzer, K. Maier, U. Kaufmann, and J. Schneider, Mater. Sci. Eng. B **29**, 61 (1994).

[7] R. Heitz, A. Hoffmann, and I. Broser, Phys. Rev. B **49**, 14 397

(1994).
[8]J. Baur, K. Maier, M. Kunzer, U. Kaufmann, J. Schneider, H. Amano, I. Akasaki, T. Detchprohm, and K. Hiramatsu, Appl. Phys. Lett. **64**, 857 (1994).
[9]C. Wetzel, D. Volm, B. K. Meyer, K. Pressel, S. Nilsson, E. N. Mokhov, and P. G. Baranov, Appl. Phys. Lett. **65**, 1033 (1994).
[10]K. Maier, M. Kunzer, U. Kaufmann, J. Schneider, B. Monemar, A. Akasaki, and H. Amano, Mater. Sci. Forum **143-147**, 93 (1994).
[11]R. Heitz, P. Thurian, I. Loa, L. Eckey, A. Hoffmann, I. Broser, K. Pressel, B. K. Meyer, and E. N. Mokhov, Appl. Phys. Lett (to be published).
[12]J. Baur, K. Maier, M. Kunzer, U. Kaufmann, and J. Schneider, Appl. Phys. Lett. **65**, 2211 (1994).
[13]J. Baur, U. Kaufmann, M. Kunzer, J. Schneider, H. Amano, I. Akasaki, T. Detchprohm, and K. Hiramatsu, Appl. Phys. Lett. **67**, 1140 (1995).
[14]Y. A. Vodakov, E. N. Mokhov, and A. D. Roenkov, Phys. Status Solidi A **51**, 209 (1979).
[15]T. Kozawa, T. Kachi, H. Kano, Y. Taya, M. Hashimoto, N. Koide, and K. Manabe, J. Appl. Phys. **75**, 1098 (1994).
[16]G. Guillot, C. Benjeddou, P. Leyral, and A. Nouailhat, J. Lumin. **31&32**, 439 (1984).
[17]B. DiBartolo, *Optical Interactions in Solids* (Wiley, New York, 1968).
[18]E. Eider, Phys. Status Solidi A **6**, K39 (1971).
[19]R. Heitz, P. Thurian, A. Hoffmann, and I. Broser, Mater. Sci. Forum **83-87**, 1247 (1992).
[20]Y. Tanabe and S. Sugano, J. Phys. Soc. Jpn. **9**, 766 (1954).
[21]D. Buhmann, H.-J. Schulz, and M. Thiede, Phys. Rev. B **19**, 5360 (1979).
[22]U. Kaufmann, H. Ennen, J. Schneider, R. Wörner, J. Weber, and F. Köhl, Phys. Rev. B **25**, 5598 (1982).
[23]M. J. Kane, M. S. Skolnick, P. J. Dean, W. Hayes, B. Cockayne, and W. R. MacEwan, J. Phys. C **17**, 6455 (1984).
[24]G. Armelles, J. Barrau, D. Thébault, and M. Brousseau, J. Phys. (Paris) **45**, 1795 (1984).
[25]G. Aszodi and U. Kaufmann, Phys. Rev. B **32**, 7108 (1985).
[26]R. Heitz, A. Hoffmann, B. Hausmann, and I. Broser, J. Lumin. **48&49**, 689 (1991).
[27]S. Gabilliet, V. Thomas, J. P. Peyrade, J. Barrau, and C. A. Bates, Phys. Lett. A **119**, 197 (1986).
[28]G. F. Imbush, W. M. Yen, A. L. Schawlow, D. E. McCumber, and M. D. Sturge, Phys. Rev. **133**, A1029 (1964).
[29]C. Benjeddou, J. H. Crasemann, G. Guillot, C. Charreaux, A. Nouhailhat, and H.-J. Schulz, J. Phys. C **20**, 2789 (1987).
[30]R. Heitz, L. Podlowski, P. Thurian, A. Hoffmann, and I. Broser, in *Proceedings of the 22nd International Conference on the Physics of Semiconductors,* edited by D. J. Lockwood (World Scientific, Singapore, 1995), p. 2379.
[31]B. Clerjaud, C. Naud, B. Deveaud, B. Lambert, B. Plot, G. Bremont, C. Benjeddou, G. Guillot, and A. Nouhailat, J. Appl. Phys. **58**, 4207 (1985).
[32]C. A. Bates, J. L. Dunn, and W. Ulrici, J. Phys. Condens. Matter **2**, 607 (1990).
[33]G. Martin, S. Strite, J. Thornton, and H. Morkoc, Appl. Phys. Lett. **58**, 2375 (1992).
[34]A. M. Hennel, C. D. Brandt, Y.-T. Wu, T. Bryskiewicz, K. Y. Ko, J. Lagowski, and H. C. Gatos, Phys. Rev. B **33**, 7353 (1986).
[35]A. M. Hennel, C. D. Brandt, K. Y. Ko, and L. M. Pawlowicz, Mater. Sci. Forum **10-12**, 645 (1986).