Zeeman spectroscopy of the Fe^{3+} center in 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 Physical-Technical Institute, 1904021 St. Petersburg, Russia

We report an optical investigation of the Zeeman behavior of the deep iron acceptor in GaN grown on 6H–SiC. The characteristic ground state splitting of the near-infrared luminescence transition at 1.2988 eV allows for an unambiguous assignment to Fe^{3+} previously proposed on the basis of ODMR results. The observed luminescence lifetime of 8 ms as well as the fine structure of the excited state are consistent with a $^4T_1(G) - {}^6A_1(S)$ transition. The $^4T_1(G)$ state is found to couple only weakly to ϵ-type phonon modes. © *1995 American Institute of Physics.*

GaN and AlN gain increasing interest in view of their potential for optoelectronic devices operating in the blue spectral region. Recent improvements of the growth techniques enabled efficient blue light-emitting diodes now being commercially available.[1] However, no electrically pumped laser based on nitrides could be demonstrated. Even though decades ago high resistivity behavior was demonstrated for Fe and Cr doped GaN layers, only recently, first detailed information on transition metal (TM) defects were reported.[2–5]

Fe is a common contamination in GaN forming a deep acceptor level suited for the generation of semi-insulating material. Recently, a structured near-infrared luminescence band with a zero-phonon line around 1.299 eV, whose position depends on the strain in the sample, was reported.[3] ODMR spectra show the clear fingerprint of a $^6A_1(S)$ ground state of an electronic d^5 configuration[2] and doping as well as electron paramagnetic resonance (EPR) experiments indicate Fe^{3+} as defect. On the basis of excitation measurements for the Fe^{3+} luminescence in GaN and AlN, Baur *et al.*[4] located the deep $Fe^{2+/3+}$ acceptor level 2.5 and 3.0 eV above the valence band, respectively,[4] resulting in estimates for valence band offsets. However, the assignment of the luminescence to an internal *d-d* transition of Fe^{3+} is based on ODMR results showing only the $^6A_1(S)$ ground state. This ODMR signal results from the nonresonant excitation process allowing for no unambiguous identification of the luminescence center. In principle, ODMR should observe directly the excited $^4T_1(G)$ state. In this letter, we report on Zeeman measurements for the zero-phonon line of the 1.3 eV luminescence band giving direct evidence for a $^6A_1(S)$ ground state.

The hexagonal *n*-type GaN samples are grown by the sublimation sandwich technique on 6H–SiC substrates and contain Fe as unintentional impurity. Luminescence is excited by the 488 nm line of an Ar^+ laser, dispersed by a 0.75 m double grating monochromator and detected with a cooled Ge photodiode. The Zeeman experiments are carried out using a 15 T split-coil superconducting magnet.

Luminescence spectra of all of our GaN samples exhibit the 1.3 eV luminescence band indicating a general contamination as defect. The shape of the luminescence accords with that reported recently.[2,3] The sample investigated in the Zeeman experiments shows the zero-phonon line at 1.2988 eV with a full width at half-maximum (FWHM) of 850 μeV [see Fig. 1(a)]. We attribute the asymmetric line shape to inhomogeneous strain in our samples. Figures 1(b) and (c) show the zero-phonon region at 8 and 14 T for magnetic field orientations $B\|c$ and $B\perp c$ (with *c* the hexagonal axis of wurzite GaN), respectively. The Zeeman behavior is anisotropic as anticipated for a trigonally coordinated point defect in
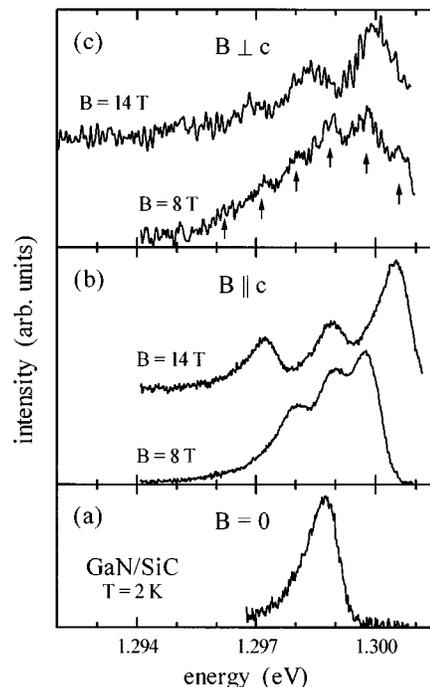

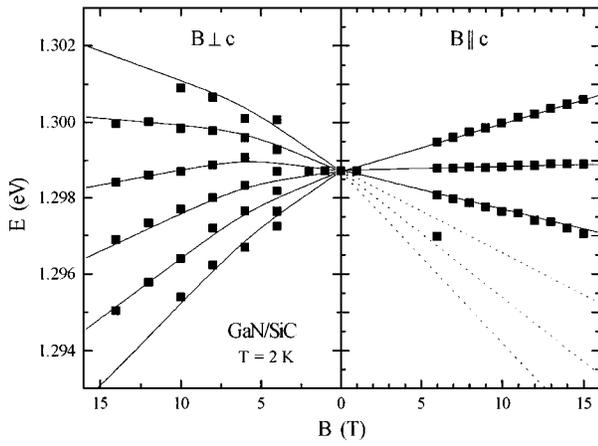FIG. 1. The zero-phonon line of the Fe^{3+} $[^4T_1(G) - {}^6A_1(S)]$ transition at $T=2$ K for $B=0$ (a), $B\|c$ (b) and $B\perp c$ (c).

FIG. 2. Zeeman splitting of the zero-phonon line of the Fe^{3+} $[^4T_1(G)$ $-^6A_1(S)]$ transition for the magnetic field orientations $B\|c$ and $B\perp c$.

hexagonal GaN. The 8 T spectrum recorded with $B\perp c$ [Fig. 1(c)] shows 6 equally spaced Zeeman components. The relative intensity of the components does not change for sample temperatures up to 10 K demonstrating the observed splitting to originate in the ground state. The sixfold splitting is clear evidence for a $^6A_1(S)$ ground state of the luminescence and therefore an electronic d^5 configuration of the luminescence center. All six components are resolved only for magnetic fields between 6 and 10 T. At higher fields the outer components become too weak and at lower fields the FWHM of the zero-phonon line exceeds the Zeeman splitting. The relative intensity of the Zeeman components critically depends on the magnetic-field orientation. For $B\perp c$ up to 6 components could be resolved whereas for $B\|c$ only three lines are observed. Qualitatively the same Zeeman behavior has been reported for the $Fe^{3+}[^4T_1(G)-^6A_1(S)]$ transition in ZnO,[6] which is a good reference material for hexagonal GaN. Both semiconductors have a wurzite structure with almost the same lattice parameters and similar band gaps. From the comparison with Fig. 3 of Ref. 6 it becomes clear that the three components observed in GaN for $B\|c$ correspond to transitions to the three lowest components of the $^6A_1(S)$ ground state ($S=5/2$). The lowest Zeeman component of the excited $^4T_1(G)$ multiplet corresponds to $S_z=-3/2$ and, thus, transitions into the $S_z=-5/2$, $-3/2$, and $-1/2$ components of the $^6A_1(S)$ ground state are expected to dominate the spectra.

Figure 2 compiles the energies of the Zeeman components observed for the zero-phonon line at 1.2988 eV. For $B\|c$ a linear Zeeman behavior is observed with the center of the sixfold splitting shifting towards lower energies, whereas for $B\perp c$ an additional nonlinear shift towards lower energies occurs. The fine structure and Zeeman behavior of the $^6A_1(S)$ ground state of an electronic d^5 configuration is described by the spin-Hamiltonian[7]

$$H = g\beta HS + \frac{a}{6}\left(S_\xi^4 + S_\eta^4 + S_\zeta^4 - \frac{707}{16}\right) + D\left(S_z^2 - \frac{35}{12}\right)$$
$$+ \frac{7F}{36}\left(S_z^4 - \frac{95}{14}S_z^2 + \frac{81}{16}\right).$$

The axial symmetry component of the C_{3v} crystal field, given by the terms proportional to D and F, lies within the z axis, the c axis of hexagonal GaN. This axis corresponds to a [111] axis in the cubic system given by ξ, η, and ζ, in which the cubic part of the crystal field is defined by a.

EPR experiments on GaN layers grown on SiC, which have been irradiated with neutrons to lower the Fermi level below the $Fe^{3+/2+}$ level, yield the following parameters for Fe^{3+} in GaN on SiC[8]

$$g_\| = 1.990 \pm 0.005,$$
$$g_\perp = 1.997 \pm 0.005,$$
$$D = (-9.32 \pm 0.06) \ \mu eV,$$
$$a = (0.60 \pm 0.06) \ \mu eV,$$
$$F = (-0.05 \pm 0.06) \ \mu eV.$$

These values are in agreement to those recently reported for GaN grown on sapphire,[2] but indicate a larger trigonal crystal field in GaN grown on 6H–SiC.

At zero magnetic field the $^6A_1(S)$ ground multiplet splits into three Kramers doublets with the $\pm 1/2$ and $\pm 3/2$ states lying 59 and 38 μeV above the $\pm 5/2$ ground state. This zero-field splitting is much too small to be resolved in our luminescence experiments. Thus, no detailed comparison of the fine structure data is possible. However, full lines in Fig. 2 represent a fit of the Zeeman data using the EPR parameter to describe the $^6A_1(S)$ ground state. Only the magnetic field dependence of the excited state has been taken variable for the fitting. Good agreement with the experimental data confirms the attribution of the 1.3 eV luminescence band to the $^4T_1(G)-^6A_1(S)$ transition of Fe^{3+} already proposed on the basis of ODMR data.[2] The excited state is found to match the behavior observed for Fe^{3+} in ZnO.[6] For $B\|c$ a linear low energy shift corresponding to a g-value of -2.81 ± 0.05 (-2.71 in case of ZnO) is observed and for $B\perp c$ the excited state behaves diamagnetic at low fields but shifts nonlinear towards lower energies at higher fields. For ZnO:Fe^{3+} and $B\perp c$ a doublet splitting of the excited component could be resolved which is hidden by the comparable large FWHM in case of GaN.

We measure a luminescence decay time of 8 ms at 1.8 K which is about twice as long as that observed at 77 K.[3] ms lifetimes are typical for the spin- and symmetry-forbidden (neglecting fine-structure interactions) $^4T_1(G)-^6A_1(S)$ transition of Fe^{3+} in semiconductors,[6,9–11] indicating a high quantum efficiency of the relaxation process. At higher sample temperatures (≈ 10 K) additional fine structure evolves on the high-energy side of the zero-phonon line due to thermal population of higher excited fine structure states of the $^4T_1(G)$ multiplet.[3] Here, we observe at least three additional components of the $^4T_1(G)$ multiplet situated 1.8, 2.6, and 3.8 meV above the lowest component at 1.2988 eV. In cubic II–VI and III–V semiconductors the fine structure of the excited $^4T_1(G)$ state is found to be reduced to a characteristic doublet with a splitting of about 1 meV.[9–11] The $^4T_1(G)$ multiplet experiences a strong Jahn–Teller coupling to ϵ-type phonon modes quenching the orbital momentum. Second-order spin-spin and spin-orbit interactions explain

the characteristic doublet structure.[12] The at least fourfold fine structure of the $^4T_1(G)$ multiplet of Fe^{3+} in hexagonal GaN indicates a softening of the Jahn–Teller coupling in trigonal symmetry. This observation supports recent results for Fe^{3+} on trigonal lattice sites in wurzite and polytypic II–VI semiconductors revealing a similar fine structure.[6,11] It should be mentioned that the transition energy of 1.2988 eV in GaN is much higher than that observed in other III–V compounds[9,10] but corresponds well to that in the wide band gap II–VI compounds[6,11] indicating a similar covalent bonding.

In conclusion we have represented a Zeeman study of the 1.2988 eV emission line in hexagonal GaN. The observed ground state splitting allows an unambiguous identification of Fe^{3+} as luminescence center. The luminescence is assigned to the $^4T_1(G) - {}^6A_1(S)$ intracenter transition.

[1] S. Nakamura, T. Mukai, and M. Senoh, Appl. Phys. Lett. **64**, 1678 (1994).

[2] K. Maier, M. Kunzer, U. Kaufmann, J. Schneider, B. Monemar, I. Akasaki, and H. Amano, Mater. Sci. Forum **143–147**, 93 (1994).

[3] 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).

[4] J. Baur, K. Maier, M. Kunzer, U. Kaufmann, and J. Schneider, Appl. Phys. Lett. **65**, 2211 (1994).

[5] K. Pressel, S. Nilsson, C. Wetzel, D. Volm, B. K. Meyer, I. Loa, P. Thurian, R. Heitz, A. Hoffmann, E. N. Mokhov, and P. G. Baranov, Mater. Sci. Technol. (to be published).

[6] R. Heitz, A. Hoffmann, and I. Broser, Phys. Rev. B **45**, 8977 (1992).

[7] B. Bleaney and R. S. Trenam, Proc. R. Soc. London Ser. A **223**, 1 (1954).

[8] M. Ludwig, Diploma thesis, Technical University Munich, 1994.

[9] K. Pressel, G. Bohnert, G. Rückert, A. Dörnen, and K. Thonke, J. Appl. Phys. **71**, 5703 (1992).

[10] K. Pressel, G. Bohnert, A. Dörnen, U. Kaufmann, J. Denzel, and K. Thonke, Phys. Rev. B **47**, 9411 (1993).

[11] A. Hoffmann, R. Heitz, and I. Broser, Phys. Rev. B **41**, 5806 (1990).

[12] P. Koidl, Phys. Status Solidi B **74**, 477 (1976).

2824   Appl. Phys. Lett., Vol. 67, No. 19, 6 November 1995

Heitz *et al.*