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Preferential substitution of Fe on physically equivalent Ga sites in GaN

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Abstract

The EPR spectra of Fe^{3+} in high-quality thick freestanding hydride vapor phase grown GaN have been studied in the X- and Q-band. A complex resonance pattern with numerous lines of different intensities provided by three different defects is observed for these nearly stress-free iron-doped samples. The dominating part is due to isolated Fe^{3+} on Ga sites and can be well described with a spin Hamiltonian (SH) with $S = \frac{5}{2}$ considering the two magnetically inequivalent Ga sites with C_{3v} symmetry in the wurtzite structure of GaN. Aside from the displacement of their magnetic axis the two Ga sites are physically equivalent. However, contrary to the expectation, we observed different Fe populations of both sites that varied from a ratio 1:4 to a ratio of nearly 1:1 in different crystals. In addition and in contrast to previously published data we determined nearly isotropic g-values and larger values for the axial fine-structure parameters D, a–F and much larger value for the cubic fine-structure parameter a.
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1. Introduction

GaN is a suitable material for spintronic applications, because after doping with Mn room temperature ferromagnetism (RT FM) has been observed. RT FM is also predicted for other TMs. The origin of ferromagnetism in $Ga_{1-x}TM_xN$ is recently discussed ([1] and references therein), but controversy can still be found in this subject matter. Saved data on the electron states and the microscopic configuration of the TM dopants in these semiconductors are essential ingredient for the explanation of the impurity-induced formation of ferromagnetic states. The electron states of GaN:Fe^{3+} and GaN:Mn^{2+} as well as of some other TMs have been studied by optical and electron paramagnetic resonance (EPR) investigations by several authors. The results up to 1998 are reviewed in Ref. [2]. Recently, new results for bulk and high-quality Mn-doped GaN grown by MBE or MOCVD were obtained by EPR, optical and other methods [3–7]. The impact of the facet types on the growth rates and impurity incorporation like Mg was observed by scanning electron microscopy and cathodoluminescence measurements [8,9]. However, as yet there are no findings about a site preference of impurity concerning the two types of Ga sites (A, B) in the GaN unit cell. These two physically equivalent sites caused by the wurtzite ABAB stacking sequence can be distinguished by EPR for electron spin systems with $S \geqslant 2$. For high-quality Mn-doped GaN grown by MBE [3] or MOCVD [7] no site splitting between the two sites could be observed due to the line width and overlapping of the allowed and forbidden hyperfine lines of the different electron spin transitions. In the case of GaN:Fe^{3+} with $S = 5/2$ the magnetic site inequivalence was observed some years ago [10,11], but the strain in the sample prevented a detailed investigation.

We present the results of EPR studies of a set of high-quality HVPE grown GaN:Fe crystals with different Fe concentration levels. The freestanding, nearly stress-free and bulk-like samples allowed us to carry out detailed EPR studies with high accuracy and without disturbing signals from the substrate material. We have analyzed the observed complex EPR spectra of these iron-doped samples including

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all allowed and forbidden transitions of the dominating spectra due to the isolated Fe^{3+}_{Ga} on the two Ga sites. Aside from the displacement of their magnetic axes the two Ga sites are physically equivalent. Therefore one would expect the Fe^{3+} impurity to show no preference for a particular Ga site and would anticipate spectra of equal intensity from both sites. However, contrary to the expectation we observed for higher Fe concentrations a marked difference in the intensity of the spectra from the two sites.

2. Experimental details

The EPR studies have been performed on a set of high-quality, 300–400 μm thick free-standing HVPE grown GaN:Fe crystals with different Fe concentration levels ranging from 2×10^{16}–$2 \times 10^{20}\,cm^{-3}$. For the EPR studies small samples with suitable dimensions for X- and Q-band measurements were cut along the main crystallographic axes. The EPR measurements were carried out using a Bruker ESP 300E spectrometer operating both in X- and Q-band. The sample temperatures in the range 3.9–300 K were achieved with Oxford Instruments continuous flow cryostats.

3. Results and discussion

The first EPR study of Fe^{3+} ($3d^5$, $S = \frac{5}{2}$) in GaN have been presented by Maier et al. [10] for about 40 μm thick GaN layers on sapphire substrate that was grown by vapor phase epitaxy (VPE). The observed EPR spectrum is shown in Fig. 1a for $B \| c$, where c is the hexagonal axis of the wurtzite GaN layer. Five fine-structure transitions $\Delta M = \pm 1$ with line positions typical for an $S = \frac{5}{2}$ ion in C_{3v} symmetry were observed. The line widths of the outer pair of fine structure transitions exceeded that of the central line. As any spread due to a mosaic structure of the GaN layer is small for this magnetic field direction, this different broadening of the five fine structure transition with the intensity ratio 5:8:9:8:5 is most probably caused by a strain-induced inhomogeneous distribution of the fine-structure constants. The available freestanding 300–400 μm thick HVPE grown GaN:Fe crystals are in contrast nearly stress free, as the weak broadening of the outer pairs of fine-structure transitions shows (Fig. 1b). The absence of larger strain in the layer was also confirmed by micro-Raman investigations. Characteristic Raman spectra around the E_2 (high) mode, whose position is sensitive to sample strain ([12] and references therein), are presented in Fig. 2 for different locations at the sample surface. The indicated position of $567\,cm^{-1}$ for the E_2 mode corresponds to the value for relaxed GaN, revealing that the samples are only marginally strained by the growth process and Fe substitution. Moreover, these free-standing samples allowed us to carry out EPR studies without the disturbing signals induced by impurities in the used substrate materials. The X-band EPR spectra of these iron-doped samples are presented for rotation of the magnetic field B within the $(1\,0\,\bar{1}\,0)$ plane in Fig. 3. The analysis described below shows that the main part of the spectra arose in fact from isolated Fe^{3+}_{Ga}. The complex angular dependence of the Fe^{3+}_{Ga} spectrum with strong variation of the line positions and intensities results from the strong mixing of the wave functions within the $S = \frac{5}{2}$ manifold due to the Zeeman energy comparable with the fine-structure splitting. Therefore, forbidden transitions ($\Delta M = \pm 2$, ± 3, ± 4, ± 5) with weaker intensities are additionally induced to the dominant five allowed fine-structure transitions ($\Delta M = \pm 1$) shown in Fig. 1a and b for $B \| c$. Moreover, several very weak Fe-related lines are detected, whose analysis for general magnetic field direction is very difficult due to the strong overlap with the strong Fe^{3+} spectrum. The majority of them are most probably caused by Fe^{3+}_{Ga}–Ga_i pairs. The study of these lines is still in progress and will be reported at a later date.

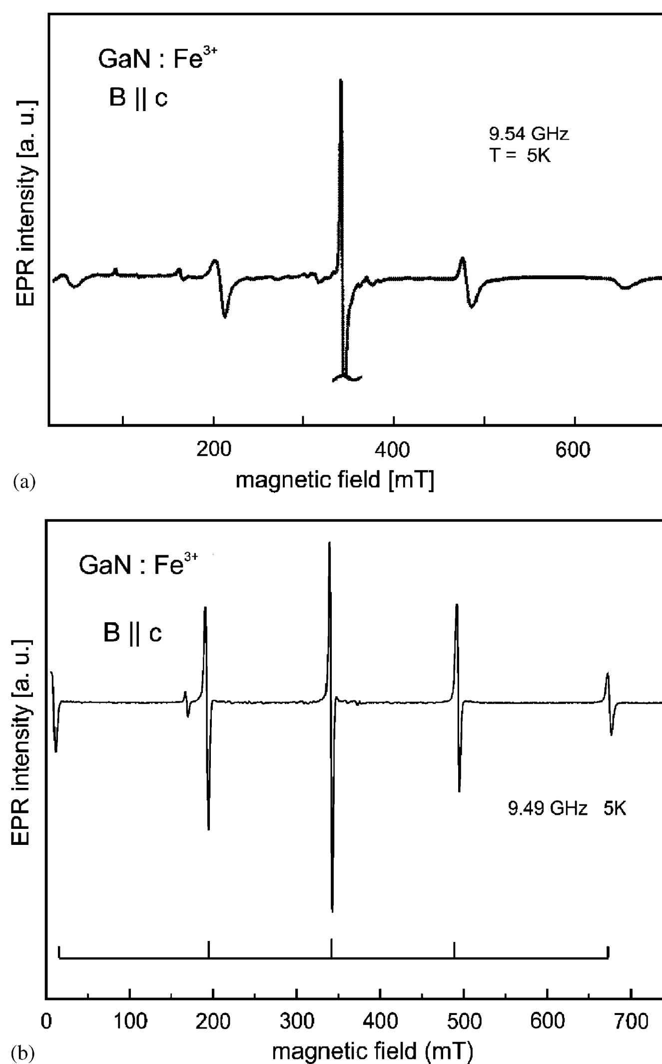

Fig. 1. X-band EPR spectra of GaN:Fe^{3+} at $B \| c$ and $T = 5\,K$ for (a) 40 μm VPE GaN layer on sapphire (after [10]) and (b) bulk-like, nearly stress-free 300 μm thick HVPE grown GaN sample and the Fe concentration in both samples is about $1 \times 10^{19}\,cm^{-3}$. The stick spectrum indicates the expected five fine-structure transitions $\Delta M = \pm 1$. The broadening of the outer fine-structure lines exhibits significant strain in the GaN layer on sapphire.

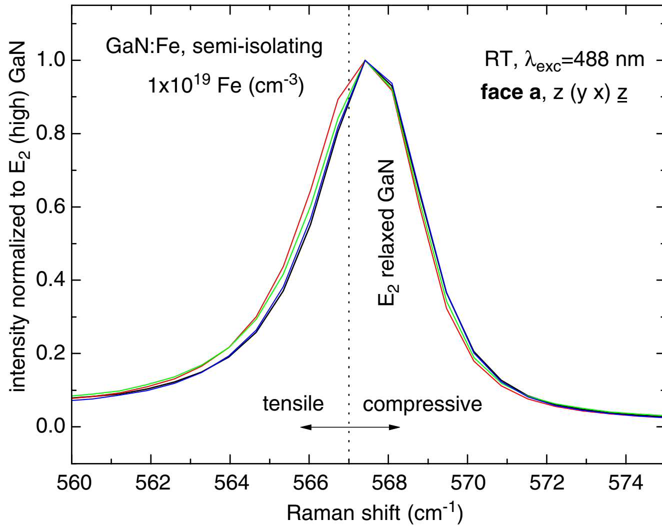

Fig. 2. Raman spectra of a 300 μm thick HVPE grown Fe-doped GaN layer with an iron concentration of $10^{19}\,cm^{-3}$ visualizing the weak shift of the E_2 (high) mode. The different solid lines represent spectra taken for different positions on the sample's surface. The samples are only weakly compressive strained. The observed shift of $\approx 0.5\,cm^{-1}$ corresponds about 0.13 GPa [12].

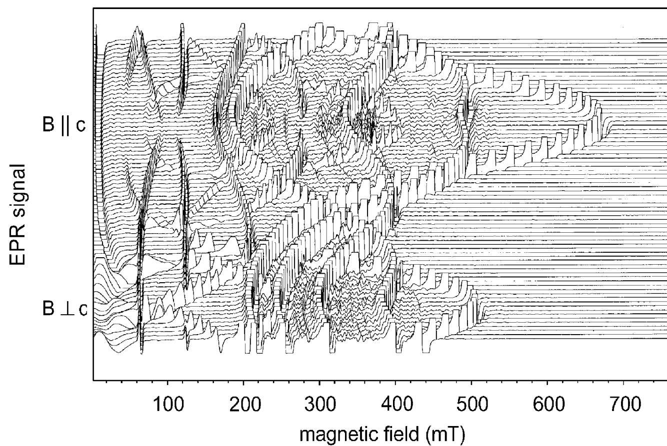

Fig. 3. Angular dependence of the EPR spectrum of Fe^{3+}_{Ga} ($S=\frac{5}{2}$) in GaN at 9.49 GHz, $T=5\,K$. Rotation of the magnetic field B in the $(1\,0\,\bar{1}\,0)$-plane between $B\|c$ and $B\perp c$ with steps of five degree. Five allowed transitions ($\Delta M=\pm1$) with high intensity and some forbidden transitions ($\Delta M=\pm2, \pm3, \pm4, \pm5$) with weak intensities are observed. In addition, numerous Fe-related very weak lines are detected. The most of them are probably caused by iron-gallium pairs.

The EPR spectrum of the isolated Fe^{3+} on Ga site with an orbital singlet ground state and $S=\frac{5}{2}$ can be well described with the spin Hamiltonian (SH) for C_{3v} symmetry

$$\mathscr{H} = \mu_B \boldsymbol{BgS} + D(S_Z^2 - 35/12) + \frac{(F-a)}{180}(70S_Z^4 - 475S_Z^2 + 2835/8) - \frac{\sqrt{2}}{36}a(S_Z(S_+^3 + S_-^3) + (S_+^3 + S_-^3)S_Z) \quad (1)$$

with $S_\pm = S_x \pm iS_y$. The crystal c-axis ([1 1 1] in cubic notation) was chosen as the quantization axis z, with the x- and y-axis being, in cubic notation, $[1\,1\,\bar{2}]$ and $[\bar{1}\,1\,0]$. The eigenvalues of the spin operators proportional D and $(F-a)$ are axial symmetric and only dependent on the angle θ between the applied external magnetic field B and the hexagonal c-axis of the GaN crystal. But the last term in Eq. (1) caused also a variation of the energy levels by rotation of the crystal at the angle ϕ around c for angles $\theta \neq 0°, 90°$. The two magnetically nonequivalent cation sites A and B with C_{3v} symmetry in the wurtzite structure are given by rotation around the c-axis by $\phi = 2k\pi/3$ and $\phi = (2k+1)\pi/3$ with $k = 0, 1, 2$ measured from the $(1\,0\,\bar{1}\,0)$ plane. The contribution of the last term in Eq. (1) is different in general crystal orientation for these two different sites and causes a splitting of the five fine-structure transitions. In the $(1\,1\,\bar{2}\,0)$ plane this splitting is absent as this plane makes equal angles with the two types of sites. When the angle θ between the c-axis and B is varied in the $(1\,0\,\bar{1}\,0)$ plane, the A and B sites will give rise tothe maximum ϕ splitting, which is maximal for $\theta = 60°$ (Fig. 4). Observing this site splitting for different FS lines at intermediate angles ($0° < \theta < 90°$) the FS parameter a and F can be determined separately. Rotation of the sample around c reflects the $\cos 3\phi$ dependence caused by the spin operators $S^3_\pm$ in Eq. (1) of the different fine-structure transitions and allows a separately determination of $|a|$ with high accuracy for $\theta = 60°$. The magnitude as well as the relative sign of the diagonal terms D and $(F-a)$ can be easily obtained at $B\|c$ where analytical solution of the eigenvalues of SH (1) exist [3]. From this fitting for $B\|c$ we obtained $\mathrm{sign}(D) = -\mathrm{sign}(a-F)$. The absolute sign of D, and hence a–F, since their relative signs are known, were found in the usual way by observing the relative intensity of the lines at $\theta = 0°$ (90°) in temperature range

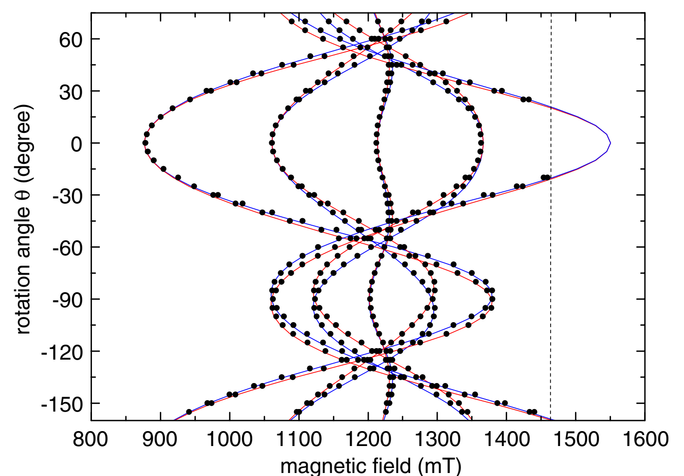

Fig. 4. Angular dependence of the experimental line positions (o) of GaN:Fe^{3+} obtained at 34 GHz and $T = 20\,K$. The magnetic field is rotated in the $(1\,\bar{2}\,1\,0)$ plane. The solid lines are calculated from the SH (1) for the Ga sites A and B with the parameters given in Table 1. (The temperature dependence of the parameters is within the error limits.)

Table 1
SH parameter for GaN:Fe^{3+} at room temperature (D, a–F, a in $10^{-4}\,cm^{-1}$)

$g_{\parallel}$	$g_{\perp}$	D	a–F	a	Reference
2.006 ± 0.002	2.006 ± 0.002	-768 ± 3	63 ± 4	78 ± 1	This work
1.990 ± 0.005	1.997 ± 0.005	-713 ± 5	52 ± 6	48 ± 5	[11][a]
1.990 ± 0.005	1.997 ± 0.005	-752 ± 5	44 ± 5	48 ± 5	[12][b]

[a] GaN epilayer of 40 μm on sapphire.
[b] Epilayer of 100–200 μm on SiC.

$T = 3.9-12$ K. The observed intensity ratio of the high-field to the low-field lines indicates that D is negative. Starting with these values the final parameter values were determined by fitting the experimental line positions obtained in the X- and Q-band for rotating the magnetic field in different crystallographic planes to the predicted ones by the numerical diagonalization of the SH (1). The results are given in Table 1 together with previous published data [10,11]. We determined isotropic g-values with an accuracy of $\Delta g = (g_{\parallel} - g_{\perp}) = 0.001$, essential larger a as well as larger D and $(a-F)$ values. The considerable deviation of the published values for the SH parameter is probably due to the essentially bigger line widths caused by the stress in the previous used samples. Besides the direct stress influence especially of the magnitude of the fine-structure parameter D, the accuracy of every fitting procedure is limited by the line width of the single EPR transition. Therefore, an accurate determination of the two g-values and the three fine-structure parameters is very difficult in the X-band, since Zeeman and fine-structure splitting are of comparable magnitude. The conducted Q-band measurements reduce the relative influence of the fine-structure splitting by an increase of the Zeeman splitting by a factor 3.5 and give evidence that the g-value is isotropic within the above given error limit.

Aside from the displacement of their magnetic axes the two Ga sites are physically equivalent. Therefore, one would expect the Fe^{3+} impurity to show no preference for a particular Ga site and one would anticipate spectra of equal intensity from both sites. However, contrary to the expectation, we observed a marked difference in the intensity of the spectra from the two sites. In fact, the intensities of these lines varied in different crystals from a ratio 1:4 to a ratio of nearly 1:1 (Fig. 5). From the measured complete angular dependence of the line positions in different crystallographic planes we can exclude the explanation that the observed intensity ratio is caused by twins. The explanation for this seeming paradox for preferred substitution for a particular Ga site obviously lies in the dynamic of the crystal growth and is probably connected with the formation of Fe^{3+}_{Ga}–Ga_i pairs mentioned above. Up to now defects associated with interstitial Ga in GaN were observed only after high-energy electron irradiation [13].

In conclusions, the ground state splitting of Fe^{3+} in Fe-doped hexagonal HVPE grown GaN has been investigated.

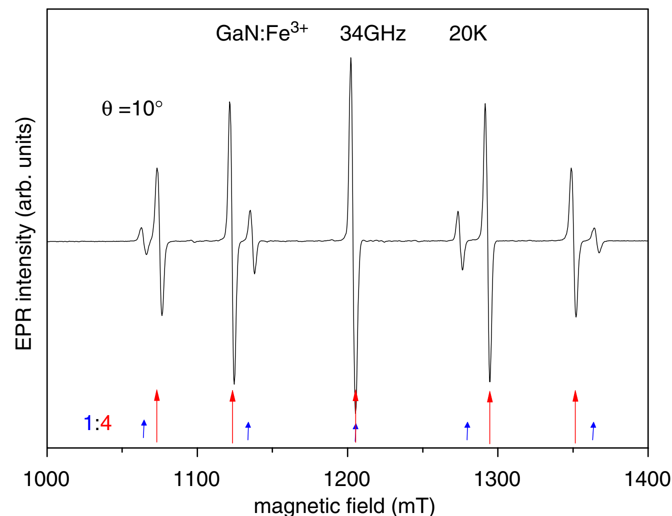

Fig. 5. Splitting of the allowed transitions (indicated by arrows) of the EPR spectrum of Fe^{3+}_{Ga} ($S = \frac{5}{2}$) in GaN at 34 GHz with the magnetic field direction B 10° from $[1 0 \bar{1} 0]$ direction in the $(1 \bar{2} 1 0)$-plane. The splitting arises from the two types of sites whose cubic axes are rotated 60° from each other about the c-axis showing the inequality of the population of both sites in the ratio 1:4 for this sample.

Improved SH parameters were obtained by EPR studies in the X- and Q-band. In addition, the studies give evidence that there exists a preferred incorporation in one of the two Ga sites.

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