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Site selectivity of Fe_{Ga}^{3+} and the formation of $Fe_{Ga}^{3+} - Ga_i$ pairs in GaN

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The electron paramagnetic resonance (EPR) spectra of Fe-related defects in high quality thick freestanding hydride vapor phase (HVPE) grown GaN have been studied in the X- and Q-band. The dominating part of the complex resonance pattern is due to isolated Fe^{3+} ($3d^5$, $S = 5/2$) on the two equivalent Ga sites A and B with C_{3V} point symmetry in the hexagonal GaN unit cell. These two physically equivalent sites, caused by the ABAB stacking sequence of the wurtzite structure, can be distinguished by EPR for electron spin systems $S \geq 2$. We found a preferential incorporation of Fe in one of the two types of Ga sites. Moreover, despite the strong overlap with the intensive Fe^{3+} transitions we could identify the main part of the additional observed very weak lines as $Fe_{Ga}^{3+} - Ga_i$ pairs.

1 Introduction

Transition metals (TMs) in GaN have been studied in detail for more than 15 years [1], but renewed interest results since Dietl et al. [2] predicted that GaN- and ZnO-based dilute magnetic semiconductors (DMS) could exhibit ferromagnetism above room temperature when heavily doped with TMs such Mn in p-type materials. Many reports indicated ferromagnetic behavior for (Ga,Mn)N, though the origin of this ferromagnetic behavior remains highly controversial ([3] and references therein). Room temperature ferromagnetism is in the meantime also observed for Fe [4] and some other TMs. A promising doping for ferromagnetic GaN is GaN:Fe co-doped with Mg [5]. The electron states of Fe- and other TM-doped GaN have been studied by optical and EPR investigations by several authors [1]. However, numerous problems, which seem important for a qualified discussion of the different models for the explanation of the observed ferromagnetism, such as exact lattice position of the substituted TMs, their energy position in the band gap for the different charge states, and, in particular their interaction with native defects in connection with higher impurity concentration are still unsolved.

In this paper we report the results of EPR studies of high quality HVPE grown Fe-doped GaN crystals. We found for Fe^{3+} a selective incorporation in one of the two physically equivalent Ga sites. The exact lattice position of the isolated Fe^{3+} is discussed. In addition, we could identify the origin of very weak lines first observed in [6].

2 Experimental details

The EPR studies have been performed on a set of high-quality, 300 to 400 μm thick freestanding HVPE grown hexagonal GaN:Fe crystals with different Fe concentration levels ranging from 2×10^{16} cm^{-3} to 2×10^{20} cm^{-3}. These samples are only marginally strained by the growth process and Fe substitution, as evidenced by the weak broadening of the outer pairs of fine-structure lines of the Fe^{3+} spectrum ($S = 5/2$)

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in comparison to the central transition $M = -1/2 \leftrightarrow 1/2$. Complete relaxations of the samples could also be confirmed by micro-Raman investigations on the base of the missing or very small shift of the E_2 (high) mode [6]. On the other hand, these freestanding samples provide the unique advantage to carry out EPR studies without the disturbing signals induced by impurities in the substrate materials.

3 Experimental results and discussion

A complex resonance pattern with numerous lines of different intensities provided by at least two different Fe-related defects has been observed for these iron-doped samples. The dominating part of the observed spectra arose from isolated Fe^{3+} ($3d^5$) on Ga sites with an orbital singlet ground state $^6A_1$. The EPR spectrum of Fe_{Ga}^{3+} can be well described with the spin Hamiltonian (SH) with $S = 5/2$ taking into account the two magnetically inequivalent Ga sites A and B with C_{3v} symmetry in the wurtzite structure of GaN [6],

$$\mathcal{H} = \mu_B \boldsymbol{B}\boldsymbol{g}\boldsymbol{S} + D\left(S_z^2 - 35/12\right) + \frac{(F-a)}{180}\left(70S_z^4 - 475S_z^2 + 2835/8\right) - \frac{\sqrt{2}}{36}a\left(S_z(S_+^3 + S_-^3) + (S_+^3 + S_-^3)S_z\right) \quad (1)$$

with $S_\pm = S_x \pm iS_y$. The crystal c-axis ([111] in cubic notation) was chosen as the quantization axis z, with the x- and y-axis being, in cubic notation, $[11\bar{2}]$ and $[\bar{1}10]$. While the eigenvalues of the first three terms in (1) are axial symmetric and dependent only on the angle θ between the magnetic field B and the c-axis of the crystal, the final term in (1) causes in addition a variation of the energy levels for rotation around c described by the angle ϕ. In general crystal orientation it contributions are different for the A and B sites and therefore the fine-structure (FS) transitions split. In the $(10\bar{1}0)$ plane this splitting is absent as this plane forms equal angles with the two types of sites (Fig. 1a). When the angle θ between the c-axis and $\boldsymbol{B}$ is varied in the $(1\bar{2}10)$ plane, the A and B sites give rise to the maximum ϕ splitting, which is maximal for θ = 60° (Fig. 1b). By fitting the experimental line positions of the FS transitions in the X- and Q-band we determined the SH parameter $g_\parallel = g_\perp = 2.006 \pm 0.002$, $D = -(768 \pm 3) \times 10^{-4}$ cm^{-1}, $a - F = (63 \pm 3) \times 10^{-4}$ cm^{-1}, and $a = (78 \pm 1) \times 10^{-4}$ cm^{-1}, which essentially differ from previous published values [7, 8]. Possible reasons for this discrepancy are discussed in [6].

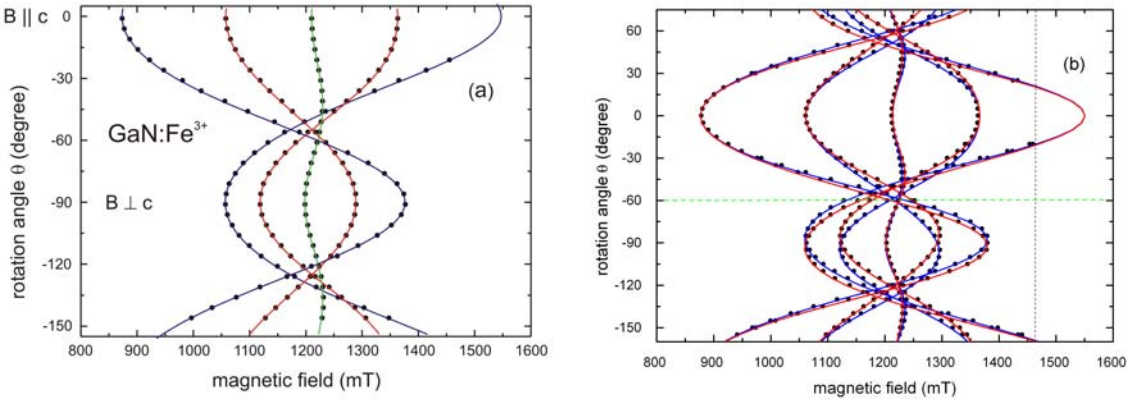

Fig. 1 (online colour at: www.pss-b.com) a), b) Road map of the experimental line positions (●) of Fe_{Ga}^{3+} ($S = 5/2$) in GaN at 34 GHz, $T = 5$ K, for rotation of the magnetic field $\boldsymbol{B}$ (a) in the $(10\bar{1}0)$ plane and (b) in the $(1\bar{2}10)$ plane. Only the five allowed transitions ($\Delta M = \pm 1$) are shown. The solid lines are calculated from the SH (1) with the parameters given in the text. For C_{3v} point symmetry of the Fe_{Ga}^{3+} site splitting between the transitions belonging to the A and B site arises only in the $(1\bar{2}10)$ plane.

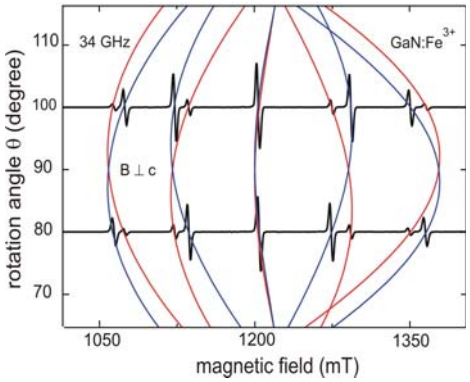

Fig. 2 (online colour at: www.pss-b.com) Splitting and intensity of the allowed fine-structure transitions of Fe^{3+}_{Ga} in hexagonal GaN at 34 GHz with the magnetic field $\boldsymbol{B}$ in the $(1\bar{2}10)$ plane $\pm 10°$ from $\boldsymbol{B} \perp \boldsymbol{c}$. The blue and red solid lines are calculated using the SH parameter given in the text. The perfect agreement between the experimental and theoretical line positions (only shown here for two angles $\pm 10°$ from $\boldsymbol{B} \perp \boldsymbol{c}$) proves that the splitting originates in fact from the sites A and B. The observed ratio of the line intensities, 1 : 4 for this sample, is determined by the inequality of the population of both sites.

The detailed analysis of the experimental angular dependencies of the Fe^{3+}_{Ga} EPR spectra for the different crystallographic planes of GaN have shown that the C_{3v} symmetry of the Ga sites is not distorted by the Fe incorporation within the given experimental accuracy, which is essentially determined by the line width of the fine-structure transitions of 2.6–3.0 mT. A lowering of the C_{3v} point symmetry would cause noticeable changes of the spectra, for instance, by a splitting of the degenerate line positions for the sites A and B for a rotation of the magnetic field $\boldsymbol{B}$ in the $(10\bar{1}0)$ plane. However, neither deviation of the calculated line positions within the experimental error limits nor such splitting is observed (Figs. 1a, b). Moreover, a simulation of the spectra with the given SH parameters also shows that a deviation of the "cubic" fine-structure axes for the sites A and B, which can be transformed by exact C_{3v} symmetry by rotation around $\boldsymbol{c}$ by $\phi = 60°$, can be excluded with an accuracy of $\Delta\phi = \pm 0.015°$. However, a displacement of the Fe^{3+} along the *c*-axis cannot be excluded, since such shift doesn't lead to a symmetry deviation. In fact, theoretical estimates of the fine-structure parameter *D* based on higher order perturbation formulas of the spin–orbit interaction are small if Fe^{3+} occupy the exact Ga^{3+} position. They suggest that Fe^{3+} is displaced by δ towards the N ligand along the lattice direction *c* reducing the Ga–N bonding by about 2% [9]. Perfect agreement of the estimated and the experimental *D* value given above is obtained for $\delta = 0.039$ Å. However, compared with other $3d^n$ theoretical predictions of the SH parameters of $3d^5$ ions are very difficult, because various mechanisms like spin–orbit interaction and intermixing from excited d^5 states contribute to the parameters with different sign. Moreover, the suggested shift δ based on calculations that are not parameter-free, refer only to the parameter *D* and do not consider the values and contributions of other fine-structure parameters *F* and *a*.

As shown above, impurities with $S \geq 2$ on the sites A and B can be distinguished from each other as the *x*-, *y*-axes of the spin operators in the final term of the SH (1) for these sites are rotated by 60° with respect to each other about the *c*-axis. Apart from these different magnetic axes systems the two sites are physically equivalent. Therefore, the substitution of impurities on both sites should take place in the same concentration, and transitions of equal intensity from both sites are expected. However, we found that the intensity ratios of these lines varied for different crystals from 1 : 4 to nearly 1 : 1 (Fig. 2). As the excellent agreement between the experimental and theoretical line positions (see Fig. 2) proves that the splitting originates in fact from the two types of substitutional sites A and B, these different line intensities can be only caused by a corresponding different iron population of the A and B sites. Up to now, only the preferential incorporation of impurities like Mg into the different facets of GaN depending on their growth rates was observed by scanning electron microscopy and cathodoluminescence measurements [10, 11]. The preferred substitution of impurities on a particular Ga site A or B was first mentioned in [6]. The explanation for this seeming paradox obviously lies in the dynamic of the crystal growth. GaN : Fe samples grown under well-defined and different growth conditions would be helpful to clarify the reasons for this observed preferred substitution.

In addition to the dominating EPR lines from the allowed and forbidden transitions of the isolated Fe^{3+}_{Ga} several very weak Fe-related lines are observed in the X- and Q-band. They strong overlap with the

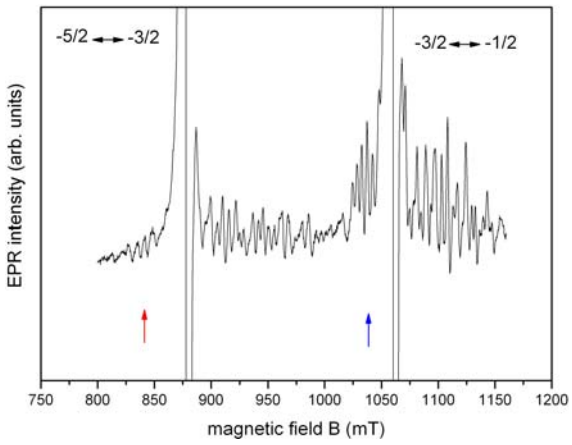

Fig. 3 (online colour at: www.pss-b.com) Part of the weak EPR spectrum of the Fe^{3+}–Ga pairs in GaN at 34 GHz for $B \| c$ and around the strong transitions $-5/2 \leftrightarrow -3/2$ and $-3/2 \leftrightarrow -1/2$ of the isolated Fe_{Ga}^{3+}. The structures indicated by red and blue arrows is reproduced by assuming a hyperfine interaction with one Ga nucleus (isotopic abundance: 60% ^{69}Ga, 40% ^{71}Ga; $\gamma^{69}/\gamma^{71} = 0.78703$, and for both, $I = 3/2$) for the Fe–Ga pair parallel to the hexagonal axis.

intensive Fe^{3+} spectrum and make an analysis very difficult [6]. However, based on the careful analysis of the isolated Fe^{3+} spectrum in the X- and Q-band, it was possible to separately extract these background lines in part. In this way we could clarify their nature and estimate some of their spin Hamiltonian parameters. We found that the majority of these weak lines arise from the different orientations of $Fe_{Ga}^{3+} - Ga_i$ pairs. Evidence for the participation of one Ga nucleus at interstitial site on this pair defect is revealed from the observed anisotropic and characteristic hyperfine interaction from a single Ga nucleus (isotopic abundance: 60% ^{69}Ga, 40% ^{71}Ga; $\gamma_n^{69}/\gamma_n^{71} = 0.78703$, and for both, $I = 3/2$). E.g., the hyperfine structures for the center orientation parallel to the *c*-axis is accurately reproduced for the different FS transitions of an $S = 5/2$ system by assuming a hyperfine constant $A_{\|}(^{71}\text{Ga}) = 39 \times 10^{-4}\,\text{cm}^{-1}$ (Fig. 3).

The small value of the hyperfine constant indicates a closed shell configuration for the Ga ion in the pair. Up to now, defects associated with interstitial Ga were observed only after high-energy electron irradiation. Two defects identified as interstitial Ga^{2+} ($3d^{10}4s^1$) in two different lattice configurations were revealed by optical detection of electron paramagnetic resonance (ODEPR) [12]. Clear evidence for the participation of one Fe^{3+} ion on the pair defect follows from the observed fine-structure line positions and their angular dependence. Both are quit similar to the corresponding ones for the isolated Fe^{3+} taking into account small changes of the fine-structure parameters and lowering of the center symmetries for center orientations not parallel to the *c*-axis. A complete analysis of this spectrum is in progress and will be published at a later date.

4 Conclusions

The dominating part of the observed complex spectra in Fe-doped hexagonal HVPE grown GaN originates from isolated Fe^{3+} on Ga site with point symmetry C_{3v}. A theoretical predicted small displacement of Fe^{3+} towards the N ligand along the lattice direction can be not excluded. A preferred incorporation of Fe^{3+} in one of the two types of physically equivalent Ga sites A and B corresponding to the ABAB stacking sequence in the hexagonal GaN structure is observed. Further studies have to clarify, if this site selectivity of Fe^{3+} substitution is connected with the proved formation of Fe–Ga pairs. A controllable preferred substitution of magnetic impurities on A or B planes in hexagonal GaN could have crucial influence on the formation of ferromagnetism.

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