Lattice sites, charge states and spin-lattice relaxation of Fe ions in $^{57}\text{Mn}^+$ implanted GaN and AlN

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Abstract

The lattice sites, valence states, resulting magnetic behaviour and spin-lattice relaxation of Fe ions in GaN and AlN were investigated by emission Mössbauer spectroscopy following the implantation of radioactive $^{57}\text{Mn}^+$ ions at ISOLDE/CERN. Angle dependent measurements performed at room temperature on the 14.4 keV γ -rays from the ^{57}Fe Mössbauer state (populated from the ^{57}Mn β^- decay) reveal that the majority of the Fe ions are in the 2+ valence state nearly substituting the Ga and Al cations, and/or associated with vacancy type defects. Emission Mössbauer spectroscopy experiments conducted over a temperature range of 100-800 K show the presence of magnetically-split sextets in the “wings” of the spectra for both materials. The temperature dependence of the sextets relate these spectral features to paramagnetic Fe^{3+} with rather slow spin-lattice relaxation rates which

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follow a T^2 temperature dependence characteristic of a two-phonon Raman process.

Keywords: GaN, AlN, Fe, Mn, ion implantation, emission Mössbauer Spectroscopy, paramagnetism

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1. Introduction

Group III-nitrides and alloys find in their crystal structure, optical emission/absorption properties and mobilities of charge carriers promises for a wide range of technological applications. III-N based devices are currently employed in optoelectronic and high frequency systems such as laser and light emitting diodes, monolithic microwave integrated circuits and high power field effect transistors for satellite and terrestrial communication and light emitting diodes[1–4]. Duly acknowledging the technological usefulness of GaN is the award of the 2014 Nobel Prize in Physics for the development of GaN-based blue light emitting diodes[5].

Several reviews [6–13] have reported experimental evidence of different forms of magnetism in TM doped GaN and AlN and their corresponding origins. In addition, our series of recent emission Mössbauer spectroscopy (eMS) investigations, following the implantation of radioactive $^{57}\text{Mn}^+$ ions on ZnO and other metal oxides[14–19] reveal magnetic components in the spectra, but angle- and temperature-dependent measurements show that at the extremely low dopant levels (10^{-3} - 10^{-4} at.%) these effects are due to paramagnetic Fe^{3+} ions with surprisingly long spin-lattice relaxation times (>20 ns). Our extension of the study to Fe in GaN and AlN, following the implantation of radioactive $^{57}\text{Mn}^+$ ions, is discussed and results presented herein confirm the absence of room temperature ferromagnetism (RTFM) in III-nitrides at these low fluences.

The presence of substitutional magnetic dopants give rise to the presence of deep levels stemming from open d shell of the impurity atoms, which strongly affect the electrical, optoelectronic, photonic, and magnetics properties of doped materials. The emerging atomic arrangements are determined not only by the chemical nature of the impurity atoms but also by their location in the crystal lattice. The main focus of the paper is to identify the nature and location of $3d$ dopant ions in the GaN and AlN crystal lattices, to investigate their potential interactions with neighbouring atoms and/or defects, resulting magnetic and spin-lattice relaxation phenomena.

Mössbauer spectroscopy is particularly powerful in this regards, given its sensitivity to the charge density and distribution in the immediate environment of the probe nucleus. An attractive feature of this technique is that the ^{57}Fe Mössbauer probe nuclei are populated following the implantation of short-lived radioactive parent nuclei $^{57}\text{Mn}^+$ ($t_{1/2} = 1.5$ min), which allows implantation fluences to be kept below 3×10^{12} ions/cm², thereby preventing the formation of precipitates and the overlap of implantation induced collision cascades.

2. Experimental Details

Radioactive $^{57}\text{Mn}^+$ beams are produced at ISOLDE/CERN, following 1.4 GeV proton-induced nuclear fission in a heated uranium carbide (UC_2) target and selective ionization of $^{57}\text{Mn}^+$ ions by a multi-stage laser irradiation system[20, 21]. The singly charged ions are then accelerated to energies of 60 keV before they are mass separated to yield pure $^{57}\text{Mn}^+$ ion beams with intensities $\geq 10^8$ ions/s.

The $^{57}\text{Mn}^+$ ions were implanted into commercially available undoped GaN (5.0 μm) and AlN (1.0 μm) films grown on sapphire substrates using hydride vapour phase epitaxy (MTI Corporation, USA). In order to check the crystallinity of the materials, X-ray diffraction (XRD) measurements were performed on the films using a Phillips PW1820

diffractometer. The XRD patterns for the GaN and AlN films are displayed in Fig 1, with the peak assignments guided by the results in the literature for the corresponding materials; GaN[22–24] and AlN[25, 26] and an additional peak corresponding to the α -Al₂O₃ substrate was observed.

Fig. 1: X-ray diffraction patterns for GaN and AlN.

The samples were mounted in an implantation chamber and held with the c -axis (0001) at 30° to the beam direction during implantation. The diameter of the beam was ~ 6 mm, and the implantation fluences were kept below 3×10^{12} ions/cm². SRIM[27] calculations show that Mn dopants in the nitride films are located within a depth 90 nm, with peak concentration in the range of 25-34 nm from the surface. eMS data were collected with a parallel plate avalanche counter (PPAC) equipped with ⁵⁷Fe enriched stainless steel and graphite electrodes, mounted on a conventional velocity drive unit outside the implantation chamber at 90° relative to the beam.

eMS data were acquired at room temperature (RT) at gamma emission angles of $\theta_\gamma = 0^\circ$ and 60° to the sample c -axis over a narrow velocity scale of ± 4.5 mm/s in order to determine the lattice sites of Fe ions and their valence states. For measurements at $\theta_\gamma = 0^\circ$,

the samples were first implanted for 4 minutes at 30° to the beam direction, then rotated to face the detector $\theta_\gamma = 0^\circ$ and a new spectrum was recorded during the decay of $^{57}\text{Mn}^*$ for 4 minutes. This process was repeated several times to obtain spectra with acceptable statistics.

A temperatures series of eMS measurements was performed over a wide velocity scale of ± 12 mm/s with the samples held at temperatures between 100 and 800 K to search for magnetic effects at the probe sites and to track their thermal evolution. The isomer shift (δ) values and the velocity scale were calibrated relative to α -Fe at RT.

3. Data Analysis

The emission Mössbauer spectra of the two nitride samples collected at $\theta_\gamma = 0^\circ$ and 60° on the narrow velocity scale are shown in Figs 2 (a) and (b), respectively.

Fig. 2: Room temperature ^{57}Fe emission Mössbauer spectra obtained at emission angles of 0° and 60° relative to the sample c -axis after implantation of $^{57}\text{Mn}^+$ into GaN and AlN.

The evident angle dependence in the spectra of both samples in Fig 2 reflects the loca-

tion of the Fe probe atoms in regular lattice sites in the hosts. The intensity ratio of the two legs of a quadrupole split doublet, in an axially symmetric electric field gradient (*EFG*), is described by the equation[28, 29],

$$f(\theta) = \frac{I_{\pm 1/2 \rightarrow \pm 3/2}}{I_{\pm 1/2 \rightarrow \pm 1/2}} = \frac{3 + 3 \cos^2 \theta}{5 - 3 \cos^2 \theta}, \quad (1)$$

where, the subscripts on I represent the different nuclear transitions and θ is the angle between the principal axis of the *EFG* tensor and the gamma emission direction. The $\pm 1/2 \rightarrow \pm 3/2$ (π) and $\pm 1/2 \rightarrow \pm 1/2$ (σ) transitions gives rise to resonances with line positions at $\delta + \Delta E_Q/2$ and $\delta - \Delta E_Q/2$ on the spectrum, respectively, where ΔE_Q is the quadrupole splitting. Thus, the relative line intensities of the two legs of a doublet, allows one to determine the sign of the *EFG*.

The spectra were analysed in terms of two quadrupole split doublets D1 and D2, using the code Vinda[30] in which Voigt line shapes were employed to describe the spectral components. The angle dependence of D1 is consistent with the relationship described in Equation (1). The principal axis of the *EFG* in GaN (and AlN) is known to be parallel to the c -axis of the sample[31]. As is evident in Fig 2, the line at lower resonance velocity (higher isomer shift) shows reduced intensity in the $\theta = 0^\circ$ spectrum ($\pm 1/2 \rightarrow \pm 1/2$ transition), implying a negative value of ΔE_Q .

The fitted spectral component, D2, uses the same quadrupole split distribution model as described by Gunnlaugsson[32]. This model simulates a distribution function of three linear segments below RT and two linear segments above RT. The distribution has free coupling between the isomer shift and quadrupole splitting[18, 32]. For consistency with the observed anisotropy, D2 was assumed to have a scaled angle dependence (asymmetry) given by the equation:

$$f_{\text{obs}}(\theta) = Q \cdot [f(\theta) - 1] + 1, \quad (2)$$

where, Q is a fitting parameter representing a scaling factor for the observed angle depen-

dence of the two-segment (component) split doublet. Values of Q range from 0 to 1, with $Q = 0$ resulting in the polycrystalline case and $Q = 1$ in the single crystalline case with full polarisation of the *EFG*. The analysis yielded a Q value of 0.09(1), and $f_{\text{obs}} = 1.2(1)$ at $\theta = 0^\circ$.

A similar procedure was employed in the analysis of the AlN data, with doublets D1 and D2 described as above but with D2 represented by a two-segment quadrupole split doublet. An additional doublet, D3, with a relatively small area fraction was required to obtain good fits to the data. D3 does not show any angle dependence and is tentatively attributed to Fe probe atoms in implantation induced damage. The asymmetries of doublets D1 and D2 are more prominent in AlN than in GaN, with the spectral fits yielding higher values of $Q = 0.25(2)$ and $f_{\text{obs}} = 1.5(1)$ for D2 at $\theta = 0^\circ$. These values and the isomer shifts reflect the different environments (charge distribution and electron densities) at the probe nuclei in the two materials.

The isomer shifts of D1 in the two samples showed a temperature dependence consistent with second-order Doppler shift and in the final simultaneous analysis were restricted to follow that behaviour. The hyperfine parameters of D2 and D3 (in AlN) and the area contribution of the central components were fitted as free parameters.

In addition to the central spectral region, magnetic features are evident in the “wings” of the spectra as shown in Figs 3 and 4 for the two samples collected as a function of temperature.

These features have been analysed in terms of two sextets, labelled BT1 and BT2, with the semi-empirical Blume-Tjon[33] relaxation model, as described by Mølholt *et al.*[19], adopted to interpret the spin relaxation phenomena. This is discussed in greater detail below.

Fig. 3: ^{57}Fe emission Mössbauer spectra obtained at the temperatures indicated and an emission angle $\theta_\gamma = 60^\circ$ after implantation of $^{57}\text{Mn}^+$ into GaN.

Fig. 4: ^{57}Fe emission Mössbauer spectra obtained at the temperatures indicated and an emission angle $\theta_\gamma = 60^\circ$ after implantation of $^{57}\text{Mn}^+$ into AlN.

4. Results and Discussion

4.1. Identification of lattice sites

The spectral parameters of the quadrupole doublets extracted from the fits to the data presented in Fig 2 are listed in Table 1 while the temperature dependence of these parameters extracted from the data presented are shown in Figs 5 and 6.

Table 1: Room temperature hyperfine parameters obtained for Fe implanted in GaN and AlN.

	D1(Fe _S)		D2 (Fe _C)		D3 (Fe _D)
	GaN	AlN	GaN	AlN	AlN
δ (mm/s)	0.24(2)	0.51(2)	0.41(1)	0.69(2)	0.56(3)
ΔE_Q (mm/s)	-0.28(3)	-0.61(1)	1.21(2)	1.52(2)	2.75(4)
$\sigma_L(\delta)$ (mm/s)	0.11(2)	0.21(1)	-	-	0.04(2)
$\sigma_R(\delta)$ (mm/s)	-	-	-	-	0.18(2)

4.1.1. GaN

The component D1 is characterised by RT isomer shift and quadrupole splitting values of $\delta = 0.24(2)$ mm/s and $\Delta E_Q = -0.28(3)$ mm/s, respectively. Alves *et al.*[34], in transmission Mössbauer spectroscopy measurements, obtained values of $\delta = 0.12$ mm/s and $\Delta E_Q = 0.52$ mm/s for a doublet component which, on the basis of proton induced X-ray emission (PIXE) and Rutherford backscattering spectroscopy/channelling (RBS/C) measurements, the authors assigned to Fe atoms on substitutional Ga sites[35]. Emission channelling (EC) measurements on ^{59}Fe implanted GaN show that 80% of the probes are slightly displaced about Ga substitutional sites, with the remainder assigned to random Fe in random sites[36]. Talut *et al.*[37–39] carried out a series of conversion electron Mössbauer spectroscopy (CEMS) investigations above RT on ^{57}Fe implanted in GaN with fluences between 1×10^{16} and $1 \times 10^{17}/\text{cm}^2$. The lower fluence spectrum was characterised by two

doublets, (D_{III}) ($\delta = 0.42$ mm/s, $\Delta E_Q = 0.48$ mm/s) and D_{IV} ($\delta = 0.59$ mm/s, $\Delta E_Q = 0.71$ mm/s), and a singlet ($\delta = -0.05$ mm/s). The doublets were attributed to Fe^{3+} with three and four nearest N neighbours, respectively, and the single line to either superparamagnetic α -Fe or paramagnetic α -Fe. Approximately 24% of the Fe atoms were found to be on substitutional Ga sites (D_{IV}) while the remainder were distributed either on interstitial locations or as small precipitates. The different ΔE_Q values from our analysis could be a result of the 4-5 orders of magnitude higher fluences utilized in the TMS and CEMS measurements which would result in a more distorted environment around the probe atom. The relatively small $|\Delta E_Q| = 0.28$ mm/s that we observe for D1 is expected in a wurtzite structure, where the site point symmetry is lower than cubic. Based on the observed anisotropy and temperature dependence of the extracted hyperfine parameters, we assign the spectral component D1 to Fe(III) residing on a Ga site (Fe_s), covalently bonded to four N atoms.

Spectral component D2 is characterized by hyperfine parameters of $\delta = 0.41(1)$ mm/s and $\Delta E_Q = 1.21(2)$ mm/s, both values larger than those of D1 (Fe_s). These values, respectively, correspond to a decrease in the s -electron density at the probe nucleus, indicative of relaxation of the bonding between the Fe ions and the surrounding lattice atoms, and a loss of tetrahedral symmetry around the Fe probe atom. In addition, there is an observed angular dependence (see spectra shown in Fig 2). D2 is therefore assigned to a combination of Fe atoms near regular crystalline sites and/or associated with neighbouring nitrogen vacancy (V_N) type defects (Fe_c). Moreover, the switch from the three segment to a two-segment doublet distribution in GaN, may be due to a small fraction of Fe in isolated amorphous pockets contributing to the Fe_c component below RT.

The isomer shift of Fe_c is consistent with both Fe^{2+} and Fe^{3+} , but on the basis of the observed temperature dependence of the quadrupole splitting, the higher spin state can

Fig. 5: The temperature dependence of the quadrupole splitting of the Fe_C spectral component in AlN compared with GaN.

be excluded. In the analysis, the average quadrupole splitting of Fe_C was fitted as a free parameter and was found to follow an exponential decrease with increasing temperature, as shown in Fig 5. For Fe^{2+} ions in the high spin configuration, the quadrupole splitting is expected to follow this variation with temperature as a result of the temperature dependent population of $3d$ orbitals, as interpreted by Ingalls[40]. Furthermore, the 2+ charge state is expected for an Fe ion paired with a nitrogen vacancy (which behaves as a donor).

4.1.2. AlN

The hyperfine parameters of D1 in AlN were determined as $\delta = 0.51(2)$ mm/s and $\Delta E_\text{Q} = -0.61(1)$ mm/s, which allows attributing this component to substitutional Fe (Fe_s). Our result is consistent with the value of 0.56 mm/s obtained by Borowski *et al.*[41] for doublet D1 from their CEMS studies of high fluence (~ 12 at.%) implantation in AlN and assigned to Fe surrounded by four N atoms in the hexagonal structure of AlN. This is similar to our assignment of Fe_s in GaN where an Fe probe atom is suggested to be incorporated on a

pure substitutional site tetrahedrally coordinated with four N nearest neighbours resulting from sp^3 hybridisation in covalent bonding.

Fig. 6: The temperature dependence of the isomer shift of D1 (Fe_s) and D2 (Fe_c) in AlN.

The isomer shift of Fe_c (D2) in AlN is constant below RT, but shows a drastic decrease above RT (see Fig 6). Evidently, above RT changes are taking place in the bonding mechanism of the near substitutional Fe atoms and vacancy related defects in their vicinity. The quadrupole splitting of Fe_c shows little variation with increasing temperature, an effect most likely due to the very small change in the charge distribution around the much larger Fe probes substituting the Al atoms in closely packed environments.

The fits to the AlN eMS spectra required an additional doublet (D3) with $\Delta E_Q = 2.75(4)$ mm/s, and $\delta = 0.56(3)$ mm/s and line width of 0.68(3) mm/s. The large line width suggests that this component is due to Fe in isolated amorphous pockets (Fe_D) in the lattice which has been observed in cubic III-V[42, 43] and group IV[44–46] semiconductors following $^{57}\text{Mn}^+$ implantation.

4.1.3. On the absence of interstitial species

In the $^{57}\text{Mn}^+ \beta^-$ decay, a mean recoil energy of 40 eV (and a maximum possible value of 93 eV)[18] is imparted to the daughter ^{57}Fe nuclei. This is expected to result in a relocation of a significant fraction of Fe atoms from their implantation sites into interstitial sites in the lattice, as reported in previous eMS studies on Mn/Fe implanted silicon[47], InP[43], GaAs and GaP[42]. The literature cites inconsistent displacement energies for the host ions in GaN and AlN. From molecular dynamics investigation, Xiao *et al.*[48] estimated average displacement energies of $E_d(\text{Ga}) = 73.2$ eV and $E_d(\text{N}) = 32.4$ eV in five main crystallographic directions in GaN. On the other hand, Wendler[49] estimated displacement values of $E_d(\text{Al}) = 18.8$ eV and $E_d(\text{N}) = 22$ eV for AlN from a combination of RBS/C experiments and SRIM based calculations. However, the absence of any interstitial Fe in both GaN and AlN in our eMS data confirms that in both samples the displacement energies of the ions are significantly above 40 eV.

4.2. Paramagnetic effects and spin-lattice relaxation

Detailed fits to the “wings” of the spectra of GaN are shown in Fig 7. The magnetically split components resemble those observed in eMS studies on metal oxides[14–16, 18, 19]. The spectra are characteristic of paramagnetic Fe^{3+} ($S_z = 5/2$) ions that are in the orbital singlet state for which the spin-orbit coupling is weak and hence the spin-lattice relaxation time relatively long. The coexistence of both Fe^{2+} and Fe^{3+} charge states in GaN is in agreement with the results of Bonanni *et al.*[50, 51]. However, in our case, paramagnetic Fe^{3+} is responsible for the observed spin-lattice relaxation effects, which is tentatively assigned to Curie paramagnetism from their studies.

The electronic spin relaxation of a probe ion incorporated in a lattice proceeds via two processes: (i) spin-lattice relaxation and (ii) dipolar spin-spin interactions between a pair of paramagnetic ions. The latter spin-spin mechanism is largely temperature independent

Fig. 7: Magnified view of the emission Mössbauer spectra of $^{57}\text{Mn}^+$ implanted GaN at temperatures indicated showing the two Blume-Tjon sextets (green and brown).

and is influenced by the distance between the ions and hence depends on the concentration of paramagnetic ions in the sample[29]. At very low Fe ion concentration (10^{-4} at.%) the effective distance between neighbouring Fe atoms is about ~ 10 nm, which makes spin-spin relaxation process negligible. In eMS experiments on ZnO at varied 3d-dopant concentrations, spin-spin relaxation has been found to only emerge above a concentration of 0.2 at.%[17].

In a crystal field potential, the 6S ground state of Fe^{3+} splits into three Kramers spin doublets with $S_z = \pm 5/2, \pm 3/2$, and $\pm 1/2$, and in the limit of low spin relaxation rates each doublet produces its own Mössbauer magnetic hyperfine spectrum and experimentally a superposition of the three sextets is observed[29, 52, 53]. The temperature dependence of spin-lattice relaxation for Kramers' ions can be expressed as $\tau_r^{-1} \propto T^n$ where $n = 1, 2, 5, 7$, or 9 in distinct temperature regions[54]. According to Blume and Tjon[33], in Mössbauer spectra showing relaxation effects, the line broadening ($\Delta\Gamma$) is related to the relaxation rate (τ_r^{-1}) by the equation[18],

$$\Delta\Gamma = \frac{2\hbar c}{E_0} \tau_r^{-1}, \quad (3)$$

where $\hbar$ is the reduced Planck's constant, c is the speed of light and E_0 is the Mössbauer transition energy. As a result, increasing the temperature results in a line broadening of the sextet from which the spin-lattice relaxation rates may be determined. The minimum time required for the nucleus to sense the hyperfine field (Larmor precession time) is proportional to the energy difference between spectral lines of the sextet. As a result, as the relaxation rate increases, the sextets start to collapse in pairs (see Fig 7) beginning with the inner most lines since their Larmor precision time is longer than that of the outer lines.

The variation of the relaxation rate with temperature obtained from a simultaneous analysis of the GaN data is presented in Fig 8(a). The relaxation rates were determined

to be $1.8 \times 10^6 \text{ s}^{-1}$ at 105 K, increasing with temperature up to $8.6 \times 10^7 \text{ s}^{-1}$ at 726 K. The spin-lattice relaxation rates showed a T^2 dependence which is characteristic of a two-phonon Raman process which is expected to dominate at temperatures, $T \geq \theta_D/3$, where θ_D is the Debye temperature[15].

The same model was employed to analyse the magnetic structure and spin relaxation observed in AlN. In an initial analysis, the line broadening at each measured temperature, was set as a free parameter. This yielded unphysical results, most likely due to the limited statistics in the AlN data. Consequently, in the final analysis the spin-lattice relaxation rates were allowed to follow a temperature dependence of T^n , where n was fitted as a global parameter. This yielded a value of $n = 2.1(4)$, again consistent with a two phonon Raman process in the measured temperature range. The relaxation rates extracted for AlN are $1.2 \times 10^6 \text{ s}^{-1}$ at 105 K increasing to $7.1 \times 10^7 \text{ s}^{-1}$ at 726 K. Fig 8(b) shows, on a logarithmic scale, the T^2 dependence of the spin-lattice relaxation rate of the paramagnetic state in AlN compared with observed trends in GaN, ZnO and $\alpha\text{-Al}_2\text{O}_3$. The relaxation rate for Fe^{3+} in AlN is slightly lower than in GaN, suggesting a slower energy transfer between the probe spin and the lattice than in GaN which could be attributed to shorter and stronger bonds in AlN. The relaxation rates for GaN, AlN and $\alpha\text{-Al}_2\text{O}_3$ closely follows the expected T^2 dependence as predicted by literature[54] for a Raman process at high temperatures.

4.3. Annealing Behaviour

4.3.1. GaN

The temperature dependence of the area fractions of the spectral components for GaN is shown in Fig 9.

At the lowest temperature of our measurements (105 K), the GaN spectrum is dom-

inated by the Fe_C component (84(1)% of the total spectral area) assigned to Fe on near substitutional sites and/or associated with vacancy related defects. The remaining fraction of 16(1)% results from the magnetic components (Fe_Mag) due to high spin Fe^{3+} . A significant decrease in the area fraction of Fe_C is evident in the range 500-600 K which is in agreement with results from positron annihilation studies on 2 MeV electron irradiated Fe-incorporated GaN, reported by Saarinen *et al.*[55, 56]. These authors attributed this behaviour to mobility of Ga vacancies (V_Ga) produced by the irradiation. In addition, reduction in the root mean square (rms) displacement values with increasing annealing temperature observed in EC studies[36] supports near Fe atoms occupying perfectly substitutional sites.

The spectral component Fe_s shows a steady increase in the area fraction, from 0% to 14%, with increasing temperature up to around 600 K and thereafter remains fairly constant up to the highest temperature of 726 K.

4.3.2. AlN

The temperature dependence of the areal fractions of the spectral components are presented in Fig 10. At the temperature of 106 K, the AlN spectrum is dominated by the Fe_C component (76%), with approximately 19% contribution from the magnetic feature (Fe_Mag) and a fraction of $\sim 5\%$ from Fe atoms in implantation induced damage (Fe_D) sites. The contribution of the Fe_C component decreases to 23% at 700 K. The substitutional component (Fe_s) increases by about 6% in the temperature range of 106-306 K, accompanied by a significant decrease in the area fractions of Fe_C ($\sim 19\%$) and Fe_Mag ($\sim 6\%$) and minor changes in Fe_D . The increase in the site population of Fe_s reflects an annealing stage in the temperature interval 150-260 K, attributable to dissociation of the impurity-vacancy complexes associated with Fe_C . There is also a small decrease in the quadrupole splitting of Fe_C above RT, indicating a slower recovery of the crystalline lattice in the vicinity of

Fe probes responsible for this component. The area fraction of the substitutional component (Fe_s) increases to approximately 31% at temperatures between 306 K and 420 K, and then remains fairly constant up to 726 K. The damage component disappears around 420 K while the magnetic contribution gradually increases from about 13% to approximately 47% at temperatures above 306 K.

There is limited information in the literature on the vacancy dissociation and mobility in AlN. The decrease in the Fe_c component and the drastic changes in the isomer shift that are evident may be attributed to the dissociation of impurity-vacancy complexes coupled with the mobility of the resulting vacancies. Such a mechanism would lead to the Fe atoms moving towards substitutional sites as well as to changes in the bonding with the neighbouring lattice atoms. These vacancy complexes, their dissociation and resulting vacancies apparently do not play an active role in the observed paramagnetic and spin-lattice relaxation effects.

5. Conclusion

The charge states and lattice locations of Fe probe ions in GaN and AlN have been investigated by emission Mössbauer spectroscopy following the implantation of $^{57}\text{Mn}^+$ ions with fluences of $\sim 3 \times 10^{12}$ ions/cm². The anisotropy of the central region of the spectra and extracted hyperfine parameters allow the spectral components to be assigned to: (i) covalently bonded Fe(III) on substitutional III sublattice, tetrahedrally coordinated with four N atoms (Fe_s), and (ii) Fe^{2+} ions located near substitutional sites and associated with vacancy (V_N) type defects (Fe_c). Fe^{2+} ions are potential deep level acceptors in GaN and AlN. In addition, in AlN a small fraction of Fe probes atoms residing in implantation induced amorphous zones was observed.

A fairly significant decrease in the fraction of Fe_c sites in GaN is evident in the temperature range 500-600 K which is attributed to mobility of vacancies. In AlN two major annealing stages are observed, the first in the temperature range 160-260 K, and the second setting in at temperatures above 306 K where drastic changes in the hyperfine parameters are evident.

Magnetic structure observed in the “wings” of the spectra for both GaN and AlN lends itself to an interpretation characteristic of paramagnetic effects resulting from the presence of high spin Fe^{3+} weakly coupled to the lattice and showing slow spin-lattice relaxation. The extracted spin-lattice relaxation rates follow an approximate T^2 dependence, typical of a two-phonon Raman process, with the rate slightly higher in GaN than in AlN.

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Fig. 8: The temperature dependence of the spin-lattice relaxation rates of the Fe^{3+} paramagnetic state in (a) GaN and (b) comparison between nitrides and oxides[15] on a logarithm scale.

Fig. 9: Areal fractions of spectral components as a function of temperature, observed in the Mössbauer spectra after implantation of $^{57}\text{Mn}^+$ into GaN.

Fig. 10: Areal fractions of spectral components as a function of temperature, observed in the Mössbauer spectra after implantation of $^{57}\text{Mn}^+$ into AlN.