Defect Structures for Fe^{3+}, Mn^{2+}, and Ni^{3+} Impurities in Wuritzite GaN Crystals

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Electron paramagnetic resonance (EPR) zero-field splittings D for Mn^{2+} and Fe^{3+} in wurtzite GaN crystals are studied from high-order perturbation formulas based on the spin-orbit mechanism in both weak- and strong-field schemes. From these studies it can be seen that the Mn^{2+} or Fe^{3+} impurity does not occupy the exact Ga^{3+} position, but is displaced by ΔR on the C_3 axis. The displacements are confirmed from a study of the superposition model, based on which a normal value of $\overline{b_2}(R_0)$ ($\approx$ –0.34 (15) cm^{-1}) for the Fe^{3+}-N^{3-} combination is suggested. The EPR parameters D, $g_{\|}$ and $g_{\perp}$ for Ni^{3+} in GaN crystals are also studied. It is found that Ni^{3+} is almost not displaced. The impurity displacements in GaN are discussed by considering the valences and radii of these impurity ions and the replaced Ga^{3+} ion. – Pacs: 61.16Hn; 76.30Fc; 71.70Ch

Key words: Defect Structure; EPR; Crystal Field Theory; GaN; Fe^{3+}; Mn^{2+}; Ni^{3+}.

1. Introduction

The wide band gap semiconductor GaN is currently the subject of the extensive research due to its technological significance in the production of light emitting devices, photodetectors and high power electronics [1 - 3]. Synthesis of high purity GaN can be inhibited by uncontrolled introduction of impurities, in particular transition-metal impurities during the growth and post-growth processing. Since transition metal impurities can play an important role in the control of the electrical and optical properties of materials, many spectroscopic methods have been used to detect and study these impurities in GaN crystals and epitaxial films. For example, the EPR parameters (zero-field splitting D and g factors) of $3d^5$ ions Fe^{3+}, Mn^{2+} and $3d^7$ ion Ni^{3+} in wurtzite GaN crystals were measured [4, 5]. However, no theoretical studies for these EPR parameters have been made. Since the EPR parameters are sensitive to the immediate environment of paramagnetic ions, a theoretical study of the EPR parameters related to the structure can yield useful information on the defect structure for a paramagnetic impurity center. Obviously, such studies for the above impurities in GaN are not made either. In this paper, we study the EPR parameters for Fe^{3+}, Mn^{2+} and Ni^{3+} ions in GaN crystals from high-order perturbation formulas. From these studies, the EPR parameters are explained reasonably.

2. Calculations

2.1. Zero-field Splittings of Fe^{3+} and Mn^{2+} in GaN

Although there are several microscopic mechanisms which contribute to zero-field splittings of $3d^5$ ions in crystals, the spin-orbit coupling mechanism is regarded as the dominant one [6 - 7]. For example, the spin-lattice coupling coefficients G_{11} and G_{44} (which are related to the stress dependence of zero-field splitting) for Fe^{3+} in GaP and InP are reasonably explained from the high-order perturbation formulas of zero-field splitting based on the spin-orbit coupling mechanism in the weak-field scheme [8]. The formula is also suitable for the calculation of zero-field splittings for Fe^{3+} and Mn^{2+} in GaN. The high-order perturbation formulas based on the spin-orbit coupling mechanism for an S-state ion can also be derived by the strong-field scheme [7], as done by Macfarlane for F-state ions [9]. In the following, we study the defect structures of Fe^{3+} and Mn^{2+} in GaN by calculating the zero-field splitting from the high-order perturbation formulas in both the weak- and strong-field schemes.

According to the spin-orbit coupling mechanism in the weak-field scheme (where the total crystal field V and the spin-orbit interaction H_{SO} are taken as perturbations), the fourth-order perturbation formula of a $3d^5$ ion in trigonal symmetry can be written as [7]

$$D \approx 3\zeta^2(-B_{20}^2 - 21\zeta B_{20})/(70P^2D') \\ + \zeta^2(-10B_{40}^2 + 7B_{43}^2)/(126P^2G) \tag{1}$$

with

$$P \approx 7B+7C,\ D' \approx 17B+5C,\ G \approx 10B+5C, \tag{2}$$

where ζ is the spin-orbit coupling coefficient. B and C are the Racah parameters. From the superposition model of the crystal-field parameters [10], the trigonal field parameters B_{kl} can be given as

$$B_{20} \approx \bar{A}_2(R_0)[2(R_0/R_1)_2^t \\ + 3(3\cos^2\theta - 1)(R_0/R_1)^{t_2}],$$

$$B_{40} \approx \bar{A}_4(R_0)[8(R_0/R_1)^{t_4} \\ + 3(35\cos^4\theta - 30\cos^2\theta + 3)(R_0/R_1)^{t_2}], \tag{3}$$

$$B_{43} \approx -6\sqrt{35}\bar{A}_4(R_0)\sin^3\theta\cos\theta(R_0/R_1)^{t_2},$$

where R_1 is the bond length along the C_3 axis. θ is the angle between the bond length R_2 and C_3 axes, and t_2 and t_4 are the power-law exponents. For $3d^n$ ions, in many crystals we have t_2 ≈ 3 and $t_4 \approx 5$ [10 - 12]. $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters with the reference distance $R_0 \approx \bar{R} \approx (R_1 + 3R_2)/4$. For $3d^n$ ions in tetrahedra, $\bar{A}_4(R_0) \approx -(27/16)D_q$ [7] (where D_q is the cubic field parameter), $\bar{A}_2(R_0)/\bar{A}_4(R_0) \approx 9 \sim 12$ [11 - 13], and we take $\bar{A}_2(R_0) \approx 12\bar{A}_4(R_0)$ here.

From the perturbation calculation based on the spin-orbit coupling mechanism in the strong-field scheme (in which the cubic field V_c and the diagonal part of the free-ion Hamiltonian H_0 are taken as the unperturbated Hamiltonan and the H_{SO}, the trigonal field V_t and the off-diagonal part of H_o are the perturbation [7, 9]), the third- and fourth-order perturbation formula of a $3d^5$ ion in a trigonal field is

$$\begin{aligned} D \approx\ & (1/10)V\zeta^2(1/E_1^2 - 1/E_3^2) + (3\sqrt{2}/10)\zeta^2(1/E_1E_2 - 1/E_2E_3)V' + V[\zeta^2C(1/E_1 - 1/E_3)/(5E_1E_3) \\ & - 3\zeta^2B(1/E_1^2 - 1/E_3^2)/(5E_2) - \zeta^3[(1/E_1^2 + 1/E_3^2)/(30E_2) + 1/(10E_1E_2E_4) - 1/(15E_1E_2E_5)] \\ & - \zeta^3[1/(15E_2^2E_5) - 1/(15E_2E_3E_5) + 1/(10E_2E_3E_6) + 2(2/E_1 - 1/E_2 + 2/E_3)/(15E_2E_7)] \\ & + \sqrt{2}V'[\zeta^3(2/E_1 - 1/E_2)/(20E_2E_3) - 9\zeta^2B(1/E_1 + 1/E_3)/(5E_1E_2) - 3\zeta^2(C/E_1 - 3B/E_2)/(10E_2E_3) \\ & + \zeta^3[1/(10E_1^2E_5) + 1/(10E_1E_2E_5) + 1/(20E_2^2E_4) + 1/(20E_2^2E_6) - 1/(10E_2E_3E_5) - 1/(10E_3^2E_5) \\ & - (1/E_1E_3 + 1/E_1^2 + 1/E_3^2)/(5E_8)] + V^2\zeta^2[2/(15E_2^2E_7) + 1/(10E_1^2E_4) + 1/(15E_2^2E_5) + 1/(10E_3^2E_6)] \\ & + V'^2\zeta^2[(1/E_1^2 + 2/E_1E_3 + 1/E_3^2)/(5E_8) + 3/(10E_1^2E_5) - 3/(5E_1E_3E_5) + \zeta^2/[3/(10E_3^2E_5) \\ & + 1/(20E_2^2E_4) + 1/(20_2^2E_6) + 2/(5E_9)(2/E_1E_3 - 1/E_1^2 - 1/E_3^2)] \\ & + VV'\sqrt{2}\zeta^2(1/E_1E_4 - 1/E_1E_5 + 2/E_3E_5 + 1/E_3E_6)/(10E_2) \end{aligned} \tag{4}$$

with

$$E_1 \approx 10B + 6C - 10D_q,\quad E_2 \approx 19B + 7C,\quad E_3 \approx 10B + 6C + 10D_q,\quad E_4 \approx 18B + 6C - 10D_q, \\ E_5 \approx 13B + 5C,\quad E_6 \approx 18B + 6C + 10D_q,\quad E_7 \approx 13B + 5C,\quad E_8 \approx 14B + 5C,\quad E_9 \approx 22B + 7C. \tag{5}$$

From the superposition model [10], the trigonal field parameters V and V' can be expressed as

$$V = -(3/7)\bar{A}_2(R_0)[2(R_0/R_1)^{t_2} + 3(3\cos^2\theta - 1)(R_0/R_2)^{t_2}] - (20/63)\bar{A}_4(R_0)[(R_0/R_1)^{t_4}$$
$$+ 3(35\cos^4\theta - 30\cos^2\theta + 3)(R_0/R_2)^{t_4}] - (20\sqrt{2}/3)\bar{A}_4(R_0)\sin^3\theta\cos\theta(R_0/R_2)^{t_4},$$
$$V' = (\sqrt{2}/7)\bar{A}_2(R_0)[2(R_0/R_1)^{t_2} + 3(3\cos^2 - 1)(R_0/R_2)^{t_2}] - (5\sqrt{2}/63)\bar{A}_4(R_0)[(R_0/R_1)^{t_4}$$
$$+ 3(35\cos^4 - 30\cos^2\theta + 3)(R_0/R_2)^{t_4}] - (10/3)\bar{A}_4(R_0)\sin^3\theta\cos\theta(R_0/R_2)^{t_4} \quad (6)$$

The above perturbation formulas of splitting D in both the weak- and strong-field schemes are now applied to the studies of Fe^{3+} and Mn^{2+} in GaN.

For GaN:Fe^{3+}, from optical spectra [14] we have

$$D_q \approx -855\ \mathrm{cm}^{-1},\ B \approx 610\ \mathrm{cm}^{-1},\ C \approx 2250\ \mathrm{cm}^{-1}. \quad (7)$$

The coefficient ζ in a crystal can be estimated reasonably by the correlation [15] $\zeta \approx N^2\zeta_d^0$ with the covalency reduction factor $N^2 \approx \left[\frac{1}{2}(B/B_0 + C/C_0)\right]^{1/2}$, where ζ_d^0, B_0 and C_0 are the spin-orbit coupling coefficient and Racah parameters of a free $3d^n$ ion. For a free Fe^{3+} ion [16], $\zeta_d^0 \approx 589\ \mathrm{cm}^{-1}$, $B_0 \approx 1130\ \mathrm{cm}^{-1}$ and $C_0 \approx 4111\ \mathrm{cm}^{-1}$. The structural parameters of the host GaN are $R_1 \approx 1.952(4)$ Å, $R_2 \approx 1.951(1)$ Å and $\theta \approx 109.24(11)°$ [17 - 20]. By introducing the optical spectral parameters and the structural parameters into the above formulas, we calculate the zero-field splittings D for GaN:Fe^{3+} in both schemes. The results are compared with the observed values in Table 1.

From Table 1, one sees that the calculated values of D in both schemes are considerably different from the observed value, suggesting that the local structural parameters in the vicinity of the Fe^{3+} impurity are unlike those in the host. Since the symmetry of the Fe^{3+} center is still trigonal, for simplicity we assume that the Fe^{3+} ion in GaN does not occupy the exact substitutional position of Ga^{3+} but is displaced by ΔR on the C_3 axis (note that the displacement resulting for the smaller bond length R_1 is defined as the positive displacement direction). Thus, by fitting the calculated zero-field splittings D for both schemes to the observed value, we obtain the displacements ΔR. The results and the comparison between the calculated and observed D values are also shown in Table 1.

Table 1. The zero-field splittings D and the impurity displacements ΔR for Fe^{3+} and Mn^{2+} ions in GaN crystals.

		GaN:Fe^{3+}		GaN:Mn^{2+}	
		ΔR (Å)	D (cm^{-1}) [c]	ΔR (Å)	D (cm^{-1}) [c]
Calculation [a]	I	0	–0.011(16)	0	–0.0010(12)
	II	0.033(8)	–0.0714	0.070(4)	–0.024
Calculation [b]	I	0	0.0157(210)	0	0.0022(11)
	II	0.036(7)	–0.0715	0.082(4)	–0.024
Experiment	[4, 5]		–0.0715		–0.024

[a] Calculated from the weak-field scheme. [b] Calculated from the strong-field scheme. [c] Calculated by using the impurity displacement ΔR shown on the left side.

A similar calculation can also be made for GaN:Mn^{2+}. Although no optical spectral data of GaN:Mn^{2+} were reported, we can reasonably estimate the optical spectral parameters as

$$D_q \approx -520\ \mathrm{cm}^{-1},\ B \approx 725\ \mathrm{cm}^{-1},\ C \approx 2920\ \mathrm{cm}^{-1}. \quad (8)$$

The estimation is based on the transition energy $E(^4T_1\text{-}^6A_1) \approx 19420\ \mathrm{cm}^{-1}$ similar to AlN:Mn^{2+} [21] and the empirical correlation [22] $N^4 \approx 1 - h(L)k(M)$, where $h(L)$ is a characteristic of the ligand and $k(M)$ a characteristic of the central ion. For GaN:Mn^{2+}, $h(N^{3-}) \approx 2.4$, $k(M) \approx 0.07$ [22], and for a free Mn^{2+} ion [23], $\zeta_d^0 \approx 347\ \mathrm{cm}^{-1}$, $B_0 \approx 920\ \mathrm{cm}^{-1}$ and $C_0 \approx 3325\ \mathrm{cm}^{-1}$. Substituting these parameters into the above formulas in both schemes, the zero-field splittings D are calculated by using the structural parameters of host GaN, and the Mn^{2+} displacements in GaN:Mn^{2+} are obtained by fitting the calculated splittings D with the observed value. These results are also collected in Table 1.

2.2. EPR Parameters of Ni^{3+} in GaN

For a $3d^7$ (Ni^{3+}) ion in trigonal tetrahedral symmetry, the high-order perturbation formulas of D, $g_{\parallel}$ and $g_{\perp}$ can be given as [9, 24]

$$D \approx (2/9)\zeta^2 V(1/E_1^2 - 1/E_3^2) - \sqrt{2}\zeta^2 V'(2/3E_1E_4$$
$$+ 1/E_2E_3 + 1/3E_3E_4 + 1/E_2E_4 + 4\sqrt{2}B/E_1E_4E_5$$
$$+ 4B/E_3E_4E_5 + 9B/2E_2^2E_3), \quad (9)$$

Table 2. The EPR parameters for Ni^{3+} in GaN crystal.

	$g_{\parallel}$	$g_{\perp}$	D (cm^{-1})
Calculation	2.012	2.104	0.83(72)
Experiment [5]	2.1	2.1	≥ 1.5

$$\begin{aligned} g_{\parallel} \approx{} & g_e + 8\zeta k/3E_1^2 - 2\zeta^2(k+g_e)/3E_2^2 \\ & + 4\zeta^2(k-2g_e)/9E_3^2 + 8\zeta^2(k-2g_e)/9E_1^2 \\ & - 4\zeta^2 k/3E_1E_2 + 4\zeta^2 k/9E_1E_3 + 4\zeta^2 k/3E_2E_3 \\ & - 8\zeta kV/9E_1^2 + 8\sqrt{2}\zeta kV'/3E_1E_4, \\ g_{\perp} \approx{} & g_{\parallel} + 4\zeta kV/3E_1^2 - 4\sqrt{2}\zeta kV'/E_1E_4, \end{aligned} \tag{10}$$

where g_e (≈ 2.0023) is the spin-only value, k ($\approx N^2$) is the orbit reduction factor and E_i ($i = 1\sim 5$) are the zero-order energy denominators defined in [9] and [24]. From the transition energy $E(^4T_2\text{-}^4A_2)$ of GaN:Ni^{3+} [5] we obtain $D_q \approx 845\ \mathrm{cm}^{-1}$. For free Ni^{3+}, $B_0 \approx 1115\ \mathrm{cm}^{-1}$, $C_0 \approx 5450\ \mathrm{cm}^{-1}$ [22] and $\zeta_d^0 \approx 816\ \mathrm{cm}^{-1}$ [25]. The value of $N^4 \approx 0.4$ is estimated by fitting the calculated $g_{\parallel}$ and $g_{\perp}$ to the observed values (see Table 2), because these g factors are not sensitive to the small trigonal distortion. Thus, from these parameters and the structural parameters of the host GaN crystal, the zero-field splitting D is calculated. The result, within the calculated error arising from the errors of structural data, is close to the observed value. This suggests that the impurity displacement $\Delta R \approx 0$ in GaN:Ni^{3+} crystal.

3. Discussions

From Table 1 one sees that, to reach a good fit between theory and experiment for the zero-field splitting D, the Fe^{3+} or Mn^{2+} ion cannot occupy the exact Ga^{3+} site but is required to move by ΔR along C_3 axis. The local structural parameters in the vicinity of Fe^{3+} or Mn^{2+} in GaN are therefore different from the host ones. The displacements ΔR for Fe^{3+} or Mn^{2+} obtained from weak- and strong-field schemes are similar. It is predictable that the agreement between the displacements ΔR obtained from both schemes should be better when the order of perturbation increases. So, the perturbation formulas based on both schemes are suitable. In order to further confirm the displacements, we study the zero-field splittings D of Mn^{2+} and Fe^{3+} in GaN from the superposition model [10]. Although the model is empirical, it has proved successful in explanations of zero-field splittings (and also the crystal field parameters of $3d^5$ ions), or, on the other hand, in the studies of the local geometry of these ions in crystals from EPR data [10, 26, 27]. From this model, for a $3d^5$ ion in a trigonal MX_4 cluster, we have

$$\begin{aligned} D = b_2^0 \approx{} & \bar{b}_2(R_0)[(R_0/R_1)^{t_2} \\ & + (3/2)(3\cos^2\theta - 1)(R_0/R_2)^{t_2}], \end{aligned} \tag{11}$$

where $\bar{b}_2(R_0)$ and t_2 are equivalent to $\bar{A}_2(R_0)$ and t_2, respectively, in (3). However, their nature is unlike, so the exponent t_2 in zero-field splitting may be significantly different from that in crystal field parameters [7, 10]. For the zero-field splittings of Mn^{2+} and Fe^{3+}, $t_2 \approx 7$ [26]. The reference distance $R_0 \approx 2.1$ Å (Mn^{2+}-N^{3-} combination) [26]. Thus, from the zero-field splitting D and the structural parameters of host GaN, we obtain $\bar{b}_2(R_0) \approx 0.96\ \mathrm{cm}^{-1}$. The $\bar{b}_2(R_0)$ differs in sign and magnitude from the normal value ($\approx -0.04(2)\ \mathrm{cm}^{-1}$ for the Mn^{2+}-N^{3-} combination [26], which is obtained by combining the zero-field splittings and structural data for the $3d^5$ ion in many crystals). However, if the average Mn^{2+} displacement $\overline{\Delta R} \approx 0.075$ Å is considered, we obtain $\bar{b}_2(R_0) \approx -0.030\ \mathrm{cm}^{-1}$. The result is consistent with the normal value. So, the Mn^{2+} displacement can be regarded as reasonable. The normal value of $\bar{b}_2(R_0)$ for the Fe^{3+}-N^{3-} combination was not reported. If the reference distance R_0 (≈ 1.95 Å) of the Fe^{3+}-N^{3-} combination is taken as a typical bond distance (i. e., the sum of ionic radii of Fe^{3+} and N^{3-} [28]) and the average Fe^{3+} displacement $\overline{\Delta R}$ (≈ 0.035 Å) is applied, from the zero-field splitting of GaN:Fe^{3+}, we obtain $\bar{b}_2(R_0) \approx -0.34\ \mathrm{cm}^{-1}$ (in passing, if the displacement $\overline{\Delta R}$ is not considered, $\bar{b}_2(R_0) \approx 4.8\ \mathrm{cm}^{-1}$, which is too large to be regarded as reasonable). The $\bar{b}_2(R_0)$ value has the same sign and is by one order of magnitude larger when compared with the $\bar{b}_2(R_0)$ of the Mn^{2+}-N^{3-} combination. This is comparable with the normal values of $\bar{b}_2(R_0)$ for Mn^{2+} and Fe^{3+} with other ligands [26]. E. g., for the Mn^{2+}-O^{2-} and Fe^{3+}-O^{2-} combinations, the normal $\bar{b}_2(R_0)$ are $-0.026(10)\ \mathrm{cm}^{-1}$ and $-0.26(10)\ \mathrm{cm}^{-1}$, respectively; and for the Mn^{2+}-F^{-} and Fe^{3+}-F^{-} combinations, they are, respectively, $-0.024(2)\ \mathrm{cm}^{-1}$ and $-0.20(4)\ \mathrm{cm}^{-1}$ [26]. So, we suggest for the Fe^{3+}-N^{3-} combination, the normal value $\bar{b}_2(R_0) \approx -0.34(15)\ \mathrm{cm}^{-1}$ with $R_0 \approx 1.95$ Å. The suggestion should be further checked for the Fe^{3+}-N^{3-} combination in other crystals.

The displacements $\overline{\Delta R}$ and hence the local structural parameters are different from impurity to impurity, i. e., $\overline{\Delta R}$ is about 0.075 Å, 0.035 Å and 0 for Mn^{2+}, Fe^{3+} and Ni^{3+}, respectively. As is known, the valence and / or size mismatch is the main cause resulting in the large local lattice distortion in the vicinity of an impurity ion. Considering the ionic radii $r \approx 0.97$, 0.79, 0.74 and 0.76 Å for Mn^{2+}, Fe^{3+}, Ni^{3+}, and Ga^{3+} ions [28] and the charge of these ions, the above differences can be understood. It appears that by studying the EPR parameters, the defect structures of a paramagnetic impurity can be obtained.

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