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Theoretical studies of the g -shift for Cr^{4+} ions in GaN crystal from crystal-field and charge-transfer mechanisms

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Abstract

The assignment of the 1.193 eV zero-phonon line of the $3d^2$ ion in GaN crystal to the internal luminescence of Cr^{4+} on the Ga^{3+} site is analysed. Based on this assignment, the g -shift Δg ($=g - g_s$) of the groundstate of this luminescence is calculated by considering not only the conventional contribution due to the crystal-field mechanism, but also the contribution due to charge-transfer mechanism. The calculated result shows good agreement with the observed value, suggesting that the assignment is reasonable. The calculated Δg due to the charge-transfer mechanism is opposite in sign and 62% in magnitude, compared with that due to the crystal-field mechanism, and so it cannot be neglected. It appears that for the $3d^2$ (or $3d^n$) ion with a high valence state in crystals (particularly, in the case of the ligand having small optical electronegativity), the reasonable explanation of the g -shift should consider the contributions from both the crystal-field and charge-transfer mechanisms.

1. Introduction

GaN is considered to be one of the most promising semiconductor materials for the construction of short-wavelength emitting devices, such as blue diodes and lasers [1]. Since transition-metal impurities in semiconductors are known to be a practically unavoidable contamination and the presence of these impurities can influence the semiconductors characteristics and device performance, the identification and study of these impurities in GaN by using spectroscopy methods have attracted research interest [2–7]. A zero-phonon line (ZPL) at 1.193 eV in GaN was found using the optical spectrum measurements [3–6]. The identification of this ZPL with a $^1E \rightarrow ^3A_2$ transition of a $3d^2$ configuration is beyond question [5, 7]. However, the assignment

to Cr^{4+} [3, 4] or Ti^{2+} [5, 6] impurities (note: in this paper, the ionic notation formulated by Clerjoud [8] is used to designate the electronic arrangement of the transition-metal impurity in GaN) is discussed controversially.

Recently, Gerstmann *et al* [7] pointed out that the calculated acceptor level of Ti_{Ga} in GaN turns out to be high in the conduction band and the excited states are resonances that can hardly give rise to a ZPL with a linewidth that is below 1 meV. So, they thought that the identification of the 1.193 eV ZPL with Ti defects as assumed by some authors [5, 6] appears to be quite unlikely and that this ZPL is assigned to chromium trace impurities, $\text{Cr}_{\text{Ga}}^{4+}$ ($3d^2$). In fact, by analysing the optical spectrum data, we also think that the ZPL at 1.193 eV should be attributed to the transition of the Cr^{4+} ion on the Ga^{3+} site in GaN crystal. As is known, for the isoelectronic $3d^n$ series, such as $3d^2$ ions Ti^{2+} , V^{3+} and Cr^{4+} , in the same crystal, the cubic crystal field parameter Δ ($\approx 10 Dq$) increases with the increasing valence. For example, for Ti^{2+} , V^{3+} and Cr^{4+} in CdTe crystal, the values of Δ are, respectively, 2890, 3560 and 5000 cm^{-1} [9]. For the above $3d^2$ ions in GaN, the band position of ${}^3T_2(\text{F})$ is very close to that of ${}^1E(\text{D})$ with ZPL at 1.193 eV [5], we can estimate that $\Delta \approx 9700 \text{ cm}^{-1}$ for this $3d^2$ ion. The optical spectrum studies showed that $\Delta \approx 7540 \text{ cm}^{-1}$ for V^{3+} in GaN [10]. So, the greater Δ of the $3d^2$ ion suggests that it should have higher valence when compared with the V^{3+} ion in GaN and the ZPL at 1.193 eV can be attributed to the internal transition of the residual Cr^{4+} ion. In addition, Heitz *et al* [5] pointed out that the groundstate of the 1.193 eV luminescence of the $3d^2$ ion in GaN is obviously a spin-triplet ($S = 1$) with an isotropic g value of 1.98 ± 0.03 . Since this g value is comparable with those of Cr^{4+} in other III–V semiconductors (e.g., for $\text{GaP}:\text{Cr}^{4+}$, $g \approx 1.986$ [11] and for $\text{GaAs}:\text{Cr}^{4+}$, $g \approx 1.994$ (1) [12]), the above assumption of this $3d^2$ ion as the Cr^{4+} ion is reasonable. Based on this assumption, in this paper, we study theoretically the g -shift Δg ($=g - g_s$, where $g_s \approx 2.0023$) for a Cr^{4+} on a Ga^{3+} site in the GaN crystal. In the study, not only the conventional contribution to Δg due to the crystal-field (CF) mechanism, but also the contribution due to charge-transfer (CT) mechanism are considered. The results are discussed.

2. Calculation using crystal-field mechanism

For the $3d^n$ ion in crystals, the g -shift arises from the CF mechanism related to the influence of crystal-field excitations and the CT mechanism related to the influence of charge-transfer excitations [13, 14]. Since the energies of the CT bands are higher than the CF bands [15], their contributions to the g -shift of the groundstate are often small. So, in most cases, only the CF mechanism is considered in the studies of the g -shift. From the CF mechanism, the high-order perturbation formula of the g -shift based on a cluster approach for the $3d^2$ ion in cubic crystals is given as [16]

$$\Delta g_{CF} = -4k'_{CF}\zeta'_{CF}/E_1 - [g_s\zeta_{CF}^2 + k'_{CF}\zeta_{CF}\zeta'_{CF} - k_{CF}\zeta_{CF}^2/2]/E_1^2 - (g_s - k_{CF}/2)\zeta_{CF}^2/E_2^2 - k'_{CF}\zeta_{CF}\zeta'_{CF}/(E_1E_2) - 6B_4k'_{CF}\zeta_{CF}^2[2/(E_1E_2E_5) + 1/(E_2^2E_5)] \quad (1)$$

with

$$\begin{aligned} \zeta_{CF} &= N_t(\zeta_d^0 + \lambda_t^2\zeta_p^0/2) & \zeta'_{CF} &= (N_tN_e)^{1/2}(\zeta_d^0 - \lambda_t\lambda_e\zeta_p^0/2) \\ k_{CF} &= N_t(1 + \lambda_t^2/2) & k'_{CF} &= (N_tN_e)^{1/2}(1 - \lambda_t\lambda_e/2) & B_4 &= N_t^3N_eB_0 \end{aligned} \quad (2)$$

where E_1 , E_2 and E_5 are the energy differences defined in [16] and can be calculated from the d–d transition energy matrices. B_0 is the Racah parameter of the free $3d^2$ ion. ζ_d^0 and ζ_p^0 are the spin–orbit coupling coefficients of a free $3d^2$ ion and a free ligand ion. λ_π and λ_σ are the mixing coefficients. The normalization coefficients N_t , N_e can be obtained from the

normalization correlation [16]

$$\begin{aligned} N_t &= [1 + \lambda_\sigma^2 + \lambda_\pi^2 + 2\lambda_\sigma S_{dp}(\sigma) + 2\lambda_\pi S_{dp}(\pi)]^{-1/2} \\ N_e &= [1 + 3\lambda_\pi^2 + 6\lambda_\pi S_{dp}(\pi)]^{-1/2} \end{aligned} \quad (3)$$

with the group overlap integrals [16]

$$S_{dp}(\pi) = \langle d_t | \pi_t \rangle = \langle d_e | \pi_e \rangle / \sqrt{3} \quad S_{dp}(\sigma) = \langle d_t | \sigma_t \rangle. \quad (4)$$

For $3d^n$ ions in semiconductors, the conventional B , C and Δ scheme is not suitable and one should apply the modified N_t , N_e and Δ_{eff} scheme for studying the CF spectra [16]. For GaN:Cr^{4+} , from the optical spectra [5] and the Racah parameters $B_0 \approx 1039 \text{ cm}^{-1}$, $C_0 \approx 4238 \text{ cm}^{-1}$ for the free Cr^{4+} ion [17], we obtain $N_t \approx 0.923$, $N_e \approx 0.869$ and $\Delta_{eff} \approx 9800 \text{ cm}^{-1}$. The comparisons between the calculated and observed optical spectrum bands are shown in table 1. The integrals $S_{dp}(\pi) \approx 0.0267$ and $S_{dp}(\sigma) \approx 0.0761$ are calculated by using the Slater-type SCF functions [18, 19] and the average metal–ligand distance in the GaN crystal [20]. Thus, from (3), we obtain $\lambda_\pi \approx 0.3049$ and $\lambda_\sigma \approx 0.3502$. The g -shift due to the CF mechanism can be calculated by substituting these parameters and $\zeta_d^0(\text{Cr}^{4+}) \approx 327 \text{ cm}^{-1}$ [17] and $\zeta_p^0(\text{N}^{3-}) \approx 75 \text{ cm}^{-1}$ [21] into the above formulae. The result is compared with the observed value in table 2. From table 2, it can be seen that the g -shift cannot be explained reasonably by only using the CF mechanism.

Table 1. Optical spectra of GaN:Cr^{4+} (in units of cm^{-1}).

| 3A_2 (F)→ | 1E (D) | 3T_1 (F) | 3T_1 (P) |
|----------------|-------------|---------------|---------------|
| Calculation | 9320 | 14 000 | 22 870 |
| Experiment [5] | 9626 | 13 070 | 22 580 |

Table 2. g -shift $\Delta g (=g - g_s)$ for GaN:Cr^{4+} .

| Δg_{CF} | Δg_{CT} | Δg (total) | Δg (expt) |
|-----------------|-----------------|--------------------|--------------------------|
| -0.1123 | 0.07 | -0.0423 | -(0.0223 \pm 0.03) [5] |

3. Calculation using the charge-transfer mechanism

For isoelectronic $3d^n$ ions in crystals, because CT bands for the ions having higher valence states (e.g., the $3d^2 \text{Cr}^{4+}$ ion) are lower, their contribution to Δg may be comparable with that of CF excitations (particularly, in the cases of ligand having small optical electronegativity) and so the CT mechanism should be considered in the calculation of the g -shift [22]. In the following, we first of all derive the formula of the g -shift Δg due to the CT mechanism.

For a tetrahedral $3d^2 \text{MX}_4$ cluster, similar to the case of the $3d^5 \text{MX}_4$ cluster [23], the many-electron wavefunctions can be written in terms of eight single-electron wavefunctions out of t_2^b , t_2^a and e^n , where the superscripts b , a and n stand for ‘bonding’, ‘anti-bonding’ and ‘non-bonding’ orbitals. The groundstate 3A_2 can be expressed as

$$|{}^3A_2^1 a_2\rangle = [\theta^+ \varepsilon^+ | \xi^+ \xi^- \eta^+ \eta^- \zeta^+ \zeta^-] \quad (5)$$

where the letters on the left column are e^n orbitals and those on the right column are t_2^b orbitals. There are only two excited configurations $(e^n)^3 (t_2^b)^5$ and $(t_2^a)(e^n)^2 (t_2^b)^5$ which have a

non-vanishing spin-orbit coupling interaction with the ground 3A_2 . Thus, the ζ -components of the two 3T_2 states with $M_S = 1$ are

$$|{}^3T_2^n 1\zeta\rangle = [\theta^+ \varepsilon^+ \varepsilon^- |\xi^+ \xi^- \eta^+ \eta^- \zeta^+\rangle] \quad (6)$$

and

$$|{}^3T_2^a 1\zeta\rangle = \frac{1}{\sqrt{2}} \{ [\xi^- \theta^+ \varepsilon^+ |\xi^+ \xi^- \eta^+ \zeta^+ \zeta^-\rangle + [\eta^- \theta^+ \varepsilon^+ |\xi^+ \eta^+ \eta^- \zeta^+ \zeta^-\rangle] \}. \quad (7)$$

In the above wavefunctions of the ground and excited states, the single-electron wavefunctions can be written as

$$\begin{aligned} \psi_t^x &= N_t^x (|d_t\rangle + \lambda_\sigma^x |\sigma_t\rangle + \lambda_\pi^x |\pi_t\rangle) \\ \psi_r^x &= N_e^x (|d_e\rangle + \sqrt{3} \lambda_\pi^x |\pi_e\rangle) \end{aligned} \quad (8)$$

where $x = a$ or b , denoting the anti-bonding and bonding orbitals, as mentioned above. From the normalization relationship, we have

$$\begin{aligned} N_t^x &= [1 + (\lambda_\sigma^x)^2 + (\lambda_\pi^x)^2 + 2\lambda_\sigma^x S_{dp}(\sigma) + 2\lambda_\pi^x S_{dp}(\pi)]^{-1/2} \\ N_e^x &= [1 + 3(\lambda_\pi^x)^2 + 6\lambda_\pi^x S_{dp}(\pi)]^{-1/2}. \end{aligned} \quad (9)$$

By using the orthonormal relationship, we have

$$\begin{aligned} \lambda_\pi^b &= -\frac{1 + 3\lambda_\pi^q S_{dp}(\pi)}{3(\lambda_\pi^q + S_{dp}(\pi))} \\ \lambda_\sigma^b &= -\frac{1 + \lambda_\pi^q \lambda_\pi^b + (\lambda_\pi^q + \lambda_\pi^b) S_{dp}(\pi) + \lambda_\sigma^q S_{dp}(\sigma)}{\lambda_\sigma^q + S_{dp}(\sigma)}. \end{aligned} \quad (10)$$

It should be pointed out that the anti-bonding orbitals are those used in the cluster approach of the CF mechanism. Thus, the parameters N_t^a , N_e^a , λ_π^a and λ_σ^a are the corresponding parameters in the above CF mechanism (see section 2). The parameters λ_π^b , λ_σ^b , N_t^b and N_e^b related to the bonding orbitals can be obtained by applying the parameters of the antibonding orbitals and the overlap integrals to equations (9) and (10).

The perturbation Hamiltonian related to the CT effect is as follows

$$H'_{CT} = H_{SO}(\zeta_{CT}, \zeta'_{CT}) + H_{Ze}(k_{CT}, k'_{CT}) \quad (11)$$

where H_{SO} and H_{Ze} are the spin-orbit coupling and Zeeman terms. By using the perturbation-loop method [24, 25], we derive the second-order perturbation formula of Δg_{CT} arising from the CT effect

$$\Delta g_{CT} = 4 \left(\frac{k'_{CT} \zeta'_{CT}}{E_n} + \frac{k_{CT} \zeta_{CT}}{E_a} \right) \quad (12)$$

with

$$\begin{aligned} \zeta_{CT} &= N_t^a N_t^b \left\{ \zeta_d^0 + \left[\frac{\lambda_\pi^a \lambda_\sigma^b + \lambda_\pi^b \lambda_\sigma^a}{\sqrt{2}} - \frac{\lambda_\pi^a \lambda_\pi^b}{2} \right] \zeta_p^0 \right\} \\ \zeta'_{CT} &= N_t^b N_e^a \left\{ \zeta_d^0 + \left[\frac{\lambda_\pi^a \lambda_\sigma^b}{\sqrt{2}} + \frac{\lambda_\pi^a \lambda_\pi^b}{2} \right] \zeta_p^0 \right\} \\ k_{CT} &= N_t^a N_t^b \left\{ 1 + \left[\frac{\lambda_\pi^a \lambda_\sigma^b + \lambda_\pi^b \lambda_\sigma^a}{\sqrt{2}} - \frac{\lambda_\pi^a \lambda_\pi^b}{2} \right] + (\lambda_\sigma^a + \lambda_\sigma^b) S_{dp}(\sigma) + (\lambda_\pi^a + \lambda_\pi^b) S_{dp}(\pi) \right\} \\ k'_{CT} &= N_t^b N_e^a \left\{ 1 + \left[\frac{\lambda_\pi^a \lambda_\sigma^b}{\sqrt{2}} + \frac{\lambda_\pi^a \lambda_\pi^b}{2} \right] + \lambda_\sigma^b S_{dp}(\sigma) + (3\lambda_\pi^a + \lambda_\pi^b) S_{dp}(\pi) \right\}. \end{aligned} \quad (13)$$

Obviously, the parameters in (13) can be calculated from the above parameters. The results are

$$\zeta_{CT} \approx 127 \text{ cm}^{-1} \quad \zeta'_{CT} \approx 105 \text{ cm}^{-1} \quad k_{CT} \approx 0.380 \quad k'_{CT} \approx 0.246. \quad (14)$$

In (12), E_n and E_a are the energy differences between the excited ${}^3\text{T}_2^n$, ${}^3\text{T}_2^n$ and the ground state ${}^3\text{A}_2$. According to the ligand-field theory, we have [15]

$$E_a \approx E_n + 10 \text{ Dq}. \quad (15)$$

Since no experimental value of E_n has been reported for $\text{GaN}:\text{Cr}^{4+}$, we estimate it from an empirical formula given in [15], i.e.

$$E_n \approx 30\,000[\chi(X) - \chi(M)] \text{ cm}^{-1} \quad (16)$$

where $\chi(X)$ and $\chi(M)$ are the optical electronegativities of the ligand and $3d^n$ ions. For $\text{GaN}:\text{Cr}^{4+}$, $\chi(\text{N}^{3-}) \approx 2.8$ and $\chi(\text{Cr}^{4+}) \approx 2.65$ [15]. Thus, we obtain $E_n \approx 4500 \text{ cm}^{-1}$. The g -shift Δg_{CT} is obtained (see table 2) by substituting the value and the parameters in (14) into (12).

4. Discussion

- (1) From table 2, it can be seen that the contribution to Δg due to the CT mechanism is opposite in sign and 62% in magnitude, compared with that due to the CF mechanism, so the contribution of the CT mechanism cannot be neglected. In fact, if only the CF mechanism is considered, the calculated Δg is in poor agreement with the observed value, whereas if both the CF and CT mechanisms are considered, the calculated Δg is consistent with the observed value. To our knowledge, this is the first time that the formula for Δg_{CT} of the $3d^2$ ion arising from CT mechanism has been produced and hence has enabled the Δg arising from both the CF and CT mechanisms for the $3d^2$ ion in crystals to be calculated.
- (2) The positive sign of Δg_{CT} for the ${}^3\text{F}$ -state ($3d^2$) ion in crystals obtained in this paper is the same as that for the ${}^4\text{F}$ -state ($3d^3$) ion expected in [22]. So, the above result Δg_{CT} can be regarded as reasonable.
- (3) The above agreement of Δg between the calculation and the experiment supports the assignment of 1.193 eV ZPL to the transition of Cr^{4+} on Ga^{3+} site in the GaN crystal.

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