# EPR Parameters of the Trigonal $Fe^{+}_{Ga}$-$S_P$ Pair Defect in n-Type GaP Codoped with Iron and Sulphur

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The EPR parameters ($g$ factors $g_\parallel$, $g_\perp$, and zero-field splitting $D$) of a trigonal $Fe^{+}$ center (which is assigned to a donor-acceptor pair defect $Fe^{+}_{Ga}$-$S_P$ caused by $S^{2-}$ at a nearest-neighbor $P^{3-}$ site of an $Fe^{+}_{Ga}$ impurity) in n-type GaP codoped with iron and sulphur are calculated from high-order perturbation formulas based on the two spin-orbit coupling parameter model for the EPR parameters of a $3d^7$ ion in trigonal symmetry. The calculated results agree well with the observed values, suggesting that the assignment is suitable.

*Key words:* Electron Paramagnetic Resonance; Pair Defect; Crystal- and Ligand-field Theory; $Fe^{+}$; GaP.

## 1. Introduction

Iron-related defects in II-VI and III-V semiconductors have received considerable interest because these defects can influence the properties of these semiconductors [1 – 4]. Many optical and EPR spectra have been used to assign these defect centers. Among them, a trigonal $Fe^{+}$ center in n-type GaP codoped with iron and sulphur was found by EPR measurement, and its EPR $g$ factors $g_\parallel \approx 2.133(5)$, $g_\perp \approx 2.140(5)$ and zero-field splitting $D \approx -0.1705(3)\,\mathrm{cm}^{-1}$ were reported [3]. The $Fe^{+}$ center is assigned to a donor-acceptor $Fe^{+}_{Ga}$-$S_P$ pair defect caused by $S^{2-}$ at a nearest-neighbor $P^{3-}$ site of an $Fe^{+}_{Ga}$ impurity [3]. In order to explain these EPR parameters and to confirm the assignment of the trigonal $Fe^{+}_{Ga}$-$S_P$ center, a theoretical calculation of these EPR parameters based on the above defect model is necessary. Since the III-V semiconductors are strongly covalent, and the spin-orbit (SO) coupling parameter $\zeta^0_P$ ($\approx 250\ \mathrm{cm}^{-1}$ [5]) of ligand $P^{3-}$ is close to that ($\zeta^0_\mathrm{d} \approx 356\,\mathrm{cm}^{-1}$ [6]) of the central $3d^7$ ion $Fe^{+}$, the contribution to EPR parameters due to the admixture of $\zeta^0_\mathrm{d}$ and $\zeta^0_\mathrm{P}$ via covalence effects should be considered. Thus, a two-SO-parameter model including the contributions from both the SO coupling parameter of the central $3d^n$ ion and that of the ligand ion should be applied here [7, 8]. In this paper we calculate the EPR parameters of the $Fe^{+}_{Ga}$-$S_P$ pair defect from high-order perturbation formulas based on the two-SO-parameter model for the EPR parameters of a $3d^7$ ion in a trigonal tetrahedral site [8]. The results are discussed.

## 2. Calculation

In the two-SO-parameter model [7, 8], the one-electron basis functions are the linear combination of atomic orbitals (LCAO). For a $3d^n$ tetrahedral cluster, we have [8]

$$\begin{aligned} \Psi_\mathrm{t} &= N_\mathrm{t}(|\mathrm{d_t}\rangle + \lambda_\sigma|\sigma_\mathrm{t}\rangle + \lambda_\pi|\pi_\mathrm{t}\rangle), \\ \Psi_\mathrm{e} &= N_\mathrm{e}(|\mathrm{d_e}\rangle + \sqrt{3}\lambda_\pi|\pi_\mathrm{e}\rangle), \end{aligned} \tag{1}$$

where $|\mathrm{d}_\gamma\rangle$ ($\gamma = \mathrm{t}$ or e denotes the irreducible representation of a $T_\mathrm{d}$ group) is the d orbital of a $3d^n$ ion. $|\pi_\gamma\rangle$ and $|\sigma_\mathrm{t}\rangle$ are the p orbitals of ligands. $N_\gamma$ is the normalization coefficient and $\lambda_\sigma$ and $\lambda_\pi$ are the orbital mixing coefficients. These LCAO coefficients can be

related by the normalization relation

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

in which $S_{dp}(\sigma)$ and $S_{dp}(\pi)$ are the group overlap integrals.

From the basis functions and by using Macfarlane's perturbation-loop method [9,10], the high-order perturbation formulas of the EPR parameters for a $3d^7$ ion in trigonal $MX_4$ clusters were derived, i. e. [8],

$$\begin{aligned} D &= 2\zeta'^2(1/E_1^2-1/E_2^2)v/9 \\ &\quad +\sqrt{2}v'\zeta\zeta'[2/(3E_1E_4)+1/(E_2E_3)+1/(3E_3E_4) \\ &\qquad +1/(E_2E_4)+\sqrt{2}B_4/(E_1E_4E_5)] \\ &\quad -\sqrt{2}v'B_4\zeta'^2[4/(E_3E_4E_5)+9/(2E_2^2E_3)], \\ g_\parallel &= g_s+8k'\zeta'/(3E_1) \\ &\quad -2\zeta'(2k'\zeta-k\zeta'+2g_s\zeta')/(9E_1^2) \\ &\quad +4\zeta'^2(k-2g)/(9E_3^2)-2\zeta^2(k+g_s)/(3E_2^2) \\ &\quad +4k'\zeta'\zeta[1/(9E_1E_3)-1/(3E_1E_2)+1/(3E_2E_3)] \\ &\quad -8k'\zeta'v/(9E_1^2)+\sqrt{2}v'(k'\zeta+k\zeta')/(3E_1E_4), \\ g_\perp &= g_\parallel+4k'\zeta'v/(3E_1^2) \\ &\quad -4\sqrt{2}v'(k'\zeta+2k\zeta')/(3E_1E_4), \end{aligned} \tag{3}$$

with

$$\begin{aligned} \zeta &= (N_t)^2\left\{\zeta_d^0+\left[\sqrt{2}\lambda_\pi\lambda_\sigma-(\lambda_\pi)^2/2\right]\zeta_p^0\right\}, \\ \zeta' &= N_t\cdot N_e\left\{\zeta_d^0+\left[\lambda_\pi\lambda_\sigma/\sqrt{2}+(\lambda_\pi)^2/2\right]\zeta_p^0\right\}, \\ k &= (N_t)^2\Big[1-(\lambda_\pi)^2/2+\sqrt{2}\lambda_\pi\lambda_\sigma+2\lambda_\sigma S_{dp}(\sigma) \\ &\qquad +2\lambda_\pi S_{dp}(\pi)\Big], \\ k' &= N_t\cdot N_e\Big[1+(\lambda_\pi)^2/2+\lambda_\pi\lambda_\sigma/\sqrt{2} \\ &\qquad +4\lambda_\pi S_{dp}(\pi)+\lambda_\sigma S_{dp}(\sigma)\Big], \end{aligned} \tag{4}$$

where the zero-order energy denominators $E_i$ ($i$ = 1–5) are defined in [8]. $v$ and $v'$ are the trigonal field parameters. $g_s$ ($\approx 2.0023$) is the $g$ factor of a free ion. $\zeta_d^0$ and $\zeta_p^0$ are the SO coupling parameters of a free $3d^7$ ion and that of a free ligand ion. $B_4 = N_t^3 N_e B_0$ (the Racah parameter of a free $3d^7$ ion).

The LCAO coefficients $N_t$, $N_e$ and the effective cubic field parameter $\Delta_{eff}$ (which is close to $10Dq$) can be estimated from the optical spectra of the studied system. Since no spectral data of GaP:$Fe^+$ are reported, we estimated these parameters from the corresponding parameters of the isoelectronic $3d^7$ $Co^{2+}$ ion in GaP crystals. Since for the isoelectronic $3d^n$ ions in the same crystal the covalence and the cubic field parameter $Dq$ of $3d^n$ clusters increase with increasing valence state of the $3d^n$ ion [11], the covalence reduction factors $N_t$ and $N_e$ in GaP:$Fe^+$ should be larger and the parameter $Dq$ should be smaller than the corresponding values in GaP:$Co^{2+}$ crystal. From the values of $N_t \approx 0.85$, $N_e \approx 0.83$ and $\Delta_{eff} \approx 4120\ cm^{-1}$ in GaP:$Co^{2+}$ [12], we take $N_t \approx 0.895$, $N_e \approx 0.889$ and $\Delta_{eff} \approx 3700\ cm^{-1}$ for GaP:$Fe^+$. Since for the $Fe^{+}_{Ga}$-$S_P$ defect center in GaP the number of $P^{3-}$ ligands is three times that of $S^{2-}$ ligands, and the difference between the SO coupling parameters $\zeta_p(P^{3-}) \approx 250\ cm^{-1}$ [5] and $\zeta_p(S^{2-}) \approx 365\ cm^{-1}$ [13] is not large, we neglect the small influence of a $S^{2-}$ ion in the $P^{3-}$ site in the calculation of the parameters in (4). Thus, from the Slater-type SCF functions and the metal-ligand distance $R \approx 2.36$ Å [14] in GaP we obtain the group overlap integrals $S_{dp}(\pi) \approx 0.0137$ and $S_{dp}(\sigma) \approx -0.0422$. By applying these values to (2), we obtain $\lambda_\pi \approx -0.3114$ and $\lambda_\sigma \approx 0.4615$. Thus, the parameters in (4) can be calculated. They are $\zeta \approx 234.8\ cm^{-1}$, $\zeta' \approx 272.7\ cm^{-1}$, $k \approx 0.5614$ and $k' \approx 0.7243$.

The trigonal field parameters can be calculated from the superposition model [17], i. e.,

$$\begin{aligned} v &= \frac{6}{7}[\bar{A}_2(S)-\bar{A}_2(P)] \\ &\quad +\frac{160}{63}[\bar{A}_4(S)-\bar{A}_4(P)/27]-\frac{640}{243}\bar{A}_4(P), \\ v' &= -\frac{2\sqrt{2}}{7}[\bar{A}_2(S)-\bar{A}_2(P)] \\ &\quad +\frac{40\sqrt{2}}{63}[\bar{A}_4(S)-\bar{A}_4(P)/27]-\frac{160\sqrt{2}}{243}\bar{A}_4(P). \end{aligned} \tag{5}$$

in which $\bar{A}_2(X)$ and $\bar{A}_4(X)$ indicate the intrinsic parameters related to ligand X (X = P or S). For a tetrahedral $3d^n$ cluster, $A_4(X) \approx (27/16)Dq(X)$. The ratio $\bar{A}_2(X)/\bar{A}_4(X) \approx 9 \sim 12$ is obtained for $3d^n$ ions in many crystals, and we take $\bar{A}_2(X)/\bar{A}_4(X) \approx 9$ here. For the free $Fe^+$ ion, the Racah parameters are $B_0 \approx 869\ cm^{-1}$ and $C_0 \approx 3638\ cm^{-1}$ [6]. Thus, in the above formulas, only the value of $Dq(S^{2-})$ is not known. By fitting the calculated EPR parameters $g_\parallel$, $g_\perp$, and $D$ of the $Fe^{+}_{Ga}$-$S_P$ defect center in GaP to the experimental values, we have

$$Dq(S^{2-}) \approx 365\ cm^{-1}. \tag{6}$$

Table 1. The EPR parameters ($g$ factors $g_{\parallel}$, $g_{\perp}$, and zero-field splitting $D$) for the $Fe^{+}_{Ga}$-$S_P$ pair in GaP crystal.

| | $g_{\parallel}$ | $g$ | $D$ ($cm^{-1}$) |
|---|---|---|---|
| Calculation | 2.137 | 2.135 | −0.1720 |
| Experiment [3] | 2.133(5) | 2.140(5) | −0.1705(3) |

The calculated EPR parameters are compared with the observed values in Table 1.

## 3. Discussion

The above studies suggest that for the $Fe^{+}$-$S^{2-}$ combination in an $Fe^{+}_{Ga}$-$S_P$ center, $Dq(S^{2-}) \approx 365$ $cm^{-1}$, the value is close to that ($\approx 360$ $cm^{-1}$ [16]) for $Fe^{+}$ in a ZnS crystal and can be regarded as reasonable. Based on this, the EPR parameters $g_{\parallel}$, $g_{\perp}$, and $D$ assigned to the $Fe^{+}_{Ga}$-$S_P$ pair defect in an n-type GaP codoped with iron and sulphur can be satisfactorily explained (see Table 1). So, the assignment is suitable.

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