Calculation of the EPR Parameters and the Local Structure for Fe^+ on the Zn^{2+} Site of $ZnSiP_2$

Shao-Yi Wu[a,b], Wang-He Wei[a], and Hui-Ning Dong[b,c]

[a] Department of Applied Physics, University of Electronic Science and Technology of China,
Chengdu 610054, P. R. China
[b] International Centre for Materials Physics, Chinese Academy of Sciences,
Shenyang 110016, P.R. China
[c] College of Electronic Engineering, Chongqing University of Posts and Telecommunications,
Chongqing 400065, P.R. China

Reprint requests to S.-Y.W.; E-mail: shaoyi_wu@163.com

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The zero-field splitting D, g factors $g_\|$ and $g_\perp$ and the local structure near Fe^+ on the Zn^{2+} site of $ZnSiP_2$ are calculated from high-order perturbation formulas of the EPR parameters for a $3d^7$ ion in tetragonally distorted tetrahedra based on the cluster approach. According to these studies, we find that the impurity-ligand bonding angle α_{loc} related to the fourfold axis is about 58.05° in the studied Fe^+ impurity center, which is larger than the metal-ligand bonding angle $\alpha_h (\approx 56.65^\circ)$ in pure $ZnSiP_2$. The EPR parameters based on the above angle α_{loc} agree well with the observed values. The errors of the results are analyzed.

Key words: Electron Paramagnetic Resonance (EPR); Defect Structure; Crystal- and Ligand-field Theory; Fe^+; $ZnSiP_2$.

1. Introduction

$ZnSiP_2$ belongs to the ternary semiconductors of type II_B-IV-V_2 and I_B-III-IV_2 which have attracted attention due to their applicability in optoelectronic and nonlinear optical devices [1 – 3]. Useful properties, such as infrared absorption and reflectivity of $ZnSiP_2$ have also found interest [4, 5]. This semiconductor crystallizes in the tetragonal chalcopyrite structure, which derives directly from the cubic zincblende lattice [6]. Both the group-II_B (Zn^{2+}) and group-IV (Si^{4+}) cation sites are surrounded by tetragonally distorted phosphorus tetrahedra [6]. This sort of distortion can be regarded as a clockwise or counterclockwise rotation of the anion tetrahedron by an angle $\pm\tau$ around the fourfold axis [6, 7]. Generally, the optical and electronic properties of these semiconductors depend strongly on transition metal ions, which often act as activated impurities, and so many spectroscopical experiments have been carried out on these impurities in this type of semiconductors. For instance, the EPR spectra of Fe^+ occupying the site of the host Zn^{2+} ion in $ZnSiP_2$ were reported, and the EPR parameters zero-field splitting D and g factors $g_\|$ and $g_\perp$ were also measured [8]. Since the EPR parameters of a paramagnetic-ion in these semiconductors are sensitive to its near local structure, theoretical studies of the local structure and the EPR parameters for the tetragonal Fe^+ center in $ZnSiP_2$ may help to understand its optical and electronic properties. In the present work, the local structure and the EPR parameters for Fe^+ on the Zn^{2+} site of $ZnSiP_2$ are theoretically studied by means of high-order perturbation formulas for the EPR parameters of a $3d^7$ ion in tetragonally distorted tetrahedra.

2. Calculations

For a $Fe^+(3d^7)$ ion in a semiconductor, the contributions to the EPR parameters from the covalency and the spin-orbit (S.O.) coupling of ligands should be taken into account [9, 10]. Rather than the conventional one-S.O.-coupling-coefficient formulas without considering the contributions of ligands, two-S.O.-coupling-coefficient formulas based on the cluster approach are applied here [9, 10]. In these formulas, not only the contribution from the S.O. coupling of the central metal ion, but also that of the ligands is considered. Thus, the high-order perturbation formulas of the EPR

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parameters D, $g_{\parallel}$ and $g_{\perp}$ for a $3d^7$ ion in tetragonally distorted tetrahedra are derived. They are [11]

$$\begin{aligned} D = {} & (35/9)D_t\zeta'^2[1/E_1{}^2 - 1/E_3{}^2] \\ & - 35BD_t\zeta\zeta'/(E_2E_3{}^2), \\ g_{\parallel} = {} & g_s + 8k'\zeta'/(3E_1) \\ & - 2\zeta'(2k'\zeta - k\zeta' + 2g_sk)/(9E_1{}^2) \\ & + 4\zeta'^2(k - 2g_s)/(9E_3{}^2) - 2\zeta^2(k + g_s)/(3E_2{}^2) \\ & + k'\zeta\zeta'[4/(9E_1E_3) - 4/(3E_1E_2) + 4/(3E_2E_3)] \\ & - 140k'\zeta' D_t/(9E_1{}^2), \\ g_{\perp} = {} & g_{\parallel} + 210k'\zeta' D_t/(9E_1{}^2), \end{aligned} \tag{1}$$

where $g_s (= 2.0023)$ is the spin-only value. The denominators $E_i (i = 1-3)$ are the energy differences between the excited states ${}^4T_2$, ${}^2T_{2a}$ and ${}^2T_{2b}$ and the ground state ${}^4A_2$. They are expressed in terms of the cubic field parameter Dq and the Racah parameters B and C for the studied system:

$$\begin{aligned} & E_1 = 10Dq, \quad E_2 = 15B + 5C, \\ & E_3 = 10Dq + 9B + 3C. \end{aligned} \tag{2}$$

The S.O. coupling coefficients ζ and ζ', and the orbital reduction factors k, k' can be obtained from the cluster approach for a tetrahedral complex [11]:

$$\begin{aligned} \zeta = {} & N_t{}^2[\zeta_d{}^0 + (\sqrt{2}\lambda_\pi\lambda_\sigma - \lambda_\pi{}^2/2)\zeta_p{}^0], \\ \zeta' = {} & N_tN_e[\zeta_d{}^0 + (\lambda_\pi\lambda_\sigma/\sqrt{2} + \lambda_\pi{}^2/2)\zeta_p{}^0], \\ k = {} & N_t{}^2(1 - \lambda_\pi{}^2/2 + \sqrt{2}\lambda_\pi\lambda_\sigma + 2\lambda_\sigma S_{dp}(\sigma) \\ & + 2\lambda_\pi S_{dp}(\pi)), \\ k = {} & N_tN_e[1 + \lambda_\pi{}^2/2 + \lambda_\pi\lambda_\sigma/\sqrt{2} + 4\lambda_\pi S_{dp}(\pi) \\ & + \lambda_\sigma S_{dp}(\sigma)], \end{aligned} \tag{3}$$

where $\zeta_d{}^0$ and $\zeta_p{}^0$ are, respectively, the S.O. coupling coefficient of the d electrons of a free $3d^7$ ion, and that of the p electrons of a free ligand ion. $S_{dp}(j)$, where $j = \sigma$ or π, are the group overlap integrals. $N_\gamma(\gamma =$e and t, which stand for the irreducible representations of the T_d group) are the normalization factors and λ_j ($j = \sigma$ and π are the orbital mixing coefficients. They satisfy the normalization conditions

$$\begin{aligned} N_t = {} & [1 + \lambda_\sigma{}^2 + \lambda_\pi{}^2 + 2\lambda_\sigma S_{dp}(\sigma) \\ & + 2\lambda_\pi S_{dp}(\pi)]^{-1/2}, \\ N_e = {} & [1 + 3\lambda_\pi{}^2 + 6\lambda_\pi S_{dp}(\pi)]^{-1/2}. \end{aligned} \tag{4}$$

D_t in (1) is the tetragonal field parameter, which can be determined from the superposition model as follows [12]:

$$\begin{aligned} D_t = {} & 4\bar{A}_4(R)[7(1 - \cos^2\alpha)^2 \\ & + (35\cos^4\alpha - 30\cos^2\alpha + 3)]/21, \end{aligned} \tag{5}$$

where $\bar{A}_4(R)$ is the intrinsic parameter with the reference bonding length (or metal-ligand distance) R. For a $3d^n$ ion in tetrahedra we have $\bar{A}_4(R) \approx (27/16)Dq$ [12, 13]. α is the metal-ligand bonding angle between the direction of the distance R and the fourfold axis.

Since no optical spectra of the tetrahedral Fe^+-P^{3-} cluster were reported, we estimate the parameters N_t, N_e (which are related to the covalency factor β by the relationship $N_t{}^4 \approx N_e{}^4 \approx \beta \approx B/B_0 \approx C/C_0$ [14, 15]) and Dq from the empirical formulas [14, 15]

$$10Dq \approx f(L)g(M), \; 1 - \beta \approx h(L)k(M), \tag{6}$$

where the parameters $f(L)$ and $h(L)$ are the characteristic parameters of the ligand, and $g(M)$ and $k(M)$ the characteristic parameters of the central metal ion. For the Fe^+-P^{3-} cluster, the values $g(Fe^+)$ and $k(Fe^+)$ can be extrapolated from those of the isoelectronic Co^{2+} and Ni^{3+}, and the values $f(P^{3-})$ and $h(P^{3-})$ can also be extrapolated from those of the isoelectronic S^{2-} and Cl^-, respectively. According to the data $g(Co^{2+}) \approx 9000$ cm^{-1}, $g(Ni^{3+}) \approx 18000$ cm^{-1}, $k(Co^{2+}) \approx 0.24$, $k(Ni^{3+}) \approx 0.49$, and $f(S^{2-}) \approx 0.78$, $f(Cl^-) \approx 0.8$, $h(S^{2-}) \approx 2.7$, $h(Cl^-) \approx 2.1$ [14, 15], we obtain

$$g(Fe^+) \approx 4500 \text{ cm}^{-1}, \; k(Fe^+) \approx 0.15 \tag{7}$$

for Fe^+ and

$$f(P^{3-}) \approx 0.77, \; h(P^{3-}) \approx 3.0 \tag{8}$$

for P^{3-}. So, the optical spectral parameters $Dq \approx 350$ cm^{-1} and $\beta \approx 0.55$ can be calculated from (6). These values are comparable with those ($Dq \approx 470$ cm^{-1} and $\beta \approx 0.43$ [16]) of the isoelectronic Co^{2+}-P^{3-} cluster in GaP, where the metal-ligand distance R (≈ 2.36 Å [17]) is close to that (≈ 2.375 Å [7]) for the Zn^{2+} site in $ZnSiP_2$ of this work. This point is also consistent with the tendency that Dq decreases and the covalency factor β increases with decreasing valence of isoelectronic ions (such as $3d^2$ ions Cr^{4+}, V^{3+}, Ti^{2+} and $3d^5$ ions Fe^{3+}, Mn^{2+}) for the same ligands [14, 15]. Therefore, the spectral parameters obtained for the Fe^+ center in $ZnSiP_2$ of this work can

Table 1. The EPR parameters based on the host and local structural parameters of Fe^+ in $ZnSiP_2$.

	Host		Local		Expt.[8]
	Cal.[a]	Cal.[b]	Cal.[a]	Cal.[b]	
$g_\parallel$	2.130	2.126	2.119	2.114	2.113
$g_\perp$	2.153	2.150	2.160	2.152	2.134
D (in cm^{-1})	1.26	1.19	2.25	2.14	2.15[c]

[a] Calculation based on the one-S.O.-coupling-coefficient formulas.
[b] Calculation based on the two-S.O.-coupling-coefficient formulas.
[c] The sign of the experimental D value was not determined in [8]. The positive sign is obtained from the empirical relationship between D and $\Delta g (= g_\parallel - g_\perp)$ [24].

be regarded as reasonable. Thus, the Racah parameters B and C for the studied system can be determined from the free-ion parameters $B_0 \approx 869\ \text{cm}^{-1}$ and $C_0 \approx 3638\ \text{cm}^{-1}$ for Fe^+ [18].

By using the above metal-ligand distance R ($\approx$ 2.375 Å [7]) and the Slater-type SCF functions [19, 20], the group overlap integrals $S_{\text{dp}}(\pi) \approx 0.014$ and $S_{\text{dp}}(\sigma) \approx -0.036$ can be calculated. From (4), the mixing coefficients $\lambda_\pi \approx 0.275$ and $\lambda_\sigma \approx -0.374$ are determined. Thus, substituting the free-ion parameters $\zeta_{\text{d}}{}^0 \approx 356\ \text{cm}^{-1}$ [18] for Fe^+ and $\zeta_{\text{p}}{}^0 \approx 299\ \text{cm}^{-1}$ [21] for P^{3-} into (3), the parameters $\zeta \approx 223\ \text{cm}^{-1}$, $\zeta' \approx 256\ \text{cm}^{-1}$, $k \approx 0.631$ and $k' \approx 0.737$ are calculated.

Substituting these parameters and the host angle $\alpha_{\text{h}} (\approx 56.65^\circ$ [7]) of the Zn^{2+} site into (1), we obtain the EPR parameters D, $g_\parallel$ and $g_\perp$. The results are compared with the experiment in Table 1.

From Table 1 one finds that the calculated EPR parameters, using the host structural data, do not agree with the observed values, particularly the theoretical D value is much smaller than the experimental one. This means that the local tetragonal distortion around the impurity Fe^+ may be due, unlike that in the host crystal, to size and/or charge mismatch substitution. This point is also supported by the EPR magnetic site splitting studies of impurity ions (e.g., Mn^{2+}) on the group-II_B site in II_B-IV-V_2 semiconductors, where the local tilting angle τ_{loc} was found to be different from the host one τ_{h} [22]. The tetragonal distortion of the studied system (the impurity Fe^+ on a group-II_B Zn^{2+} site) is related to the angle α, which depends upon the tilting angle τ and the atomic position parameter x. These relationships can be expressed as [6]

$$\cos\alpha \approx \eta (16x^2 + \eta^2 + 1)^{-1/2} \tag{9}$$

and

$$\text{tg}\tau \approx (1 - 4x)/(1 + 4x), \tag{10}$$

where $\eta = c/(2a) \approx 0.966$ with the lattice constants a and c [7]. By fitting the calculated EPR parameters to the observed values, we obtain for $ZnSiP_2$:Fe^+, $\alpha_{\text{loc}} \approx 58.05^\circ$. From (9) and (10), the local tilting angle $\tau_{\text{loc}} \approx -4.8^\circ$ and the atomic position parameter $x_{\text{loc}} \approx 0.2957$ can be determined. The corresponding theoretical EPR parameters are shown in Table 1. For comparison, the calculated results by neglecting the contributions of ligands (i.e., taking $\zeta_{\text{p}}{}^0 = 0$, $\lambda_{\text{t}} = \lambda_{\text{e}} = 0$ and $N_{\text{t}} = N_{\text{e}} = \beta^{1/4}$) are also collected in Table 1.

3. Discussions

According to the above investigations, the theoretical EPR parameters based on the local tilting angle τ_{loc} for Fe^+ on the Zn^{2+} site in $ZnSiP_2$ agree better with the observed values than those based on the host angle τ_{h}. Several points may be discussed here:

1) In the host $ZnSiP_2$ the local structure parameters $\alpha_{\text{loc}} (\approx 58.05^\circ)$, $\tau_{\text{loc}} (\approx -4.8^\circ)$ and $x_{\text{loc}} (\approx 0.2957)$ obtained in this work are different from α_{h} ($\approx 56.65^\circ$, $\tau_{\text{h}} (\approx -2.1^\circ)$ and $x_{\text{h}} (\approx 0.2691)$ obtained in [7]. Since the tetragonal distortion may be characterized by the angular deviation $\Delta\alpha (= \alpha - \alpha_0$, where $\alpha_0 \approx 54.74^\circ$ is the corresponding angle for the cubic case), the local tetragonal distortion in the vicinity of the impurity Fe^+ is larger than that of the host Zn^{2+} site due to the larger tilting angle τ_{loc} of the former, induced by the size and/or charge mismatch substitution. Considering that the ionic radii are approximately 0.74 Å [23] for Zn^{2+} and Fe^{2+}, the size of the impurity Fe^+ should be larger than that of the replaced Zn^{2+} and make the local $[FeP_4]^{11-}$ cluster tighter. So, the angle α may increase a little by a further clockwise rotation of the phosphorus tetrahedron around the fourfold axis, so as to relax the local tension of the impurity center. Thus the larger angles α_{loc} and τ_{loc} for the impurity Fe^+ center compared with those for the host can be understood.

(2) For Fe^+ in $ZnSiP_2$ of this work, where the covalency is strong ($\beta \approx 0.55 \ll 1$) and the S.O. coupling coefficient ($\approx 299\ \text{cm}^{-1}$ [21]) of the ligand P^{3-} is comparable with that ($\approx 356\ \text{cm}^{-1}$ [18]) of the central Fe^+ ion, the two-S.O.-coupling-coefficient formulas based on the cluster approach should be adopted, and the contributions to the EPR parameters from the ligands cannot be neglected. If we ignore the contributions of the ligands, all the theoretical D, $g_\parallel$ and $g_\perp$ become larger than the observed values (note: although

one can fit the calculated D to the experimental result by slightly reducing τ_{loc} to about -4.5°, the theoretical g factors are still larger than the observed values). So, the two-S.O.-coupling-coefficient formulas are more reasonable than the one-S.O.-coupling-coefficient formulas in investigations of the EPR parameters for Fe^+ in $ZnSiP_2$.

(3) There are some errors in the above calculations. (i) The actual distance between the impurity Fe^+ and the ligand P^{3-} may differ somewhat from that of the metal-ligand distance R in pure $ZnSiP_2$ due to the difference between the size of the Fe^+ and that of the replaced Cd^{2+}. Fortunately, this discrepancy would only affect very slightly the group overlap integrals $S_{dp}(j)$ as well as the parameters ζ, ζ' etc. in (3). Thus, the errors of the EPR parameters and the angle α_{loc} are smaller than 0.1%, since the tetragonal distortion of the studied system depends only on the angle α (see (5)), and is almost independent of the distance R. (ii) Approximation of the parameters (i. e., g and k for Fe^+ and f and h for P^{3-} in (7) and (8)) and the empirical formulas (6) can bring errors to the value of Dq or β and hence to the final results. Based on our calculations, when these parameters vary by 10%, the errors for the EPR parameters and the angle α_{loc} are not more than 1.7%. (iii) The approximation of the model (the perturbation formulas) may also affect the results of this work. In consideration of these errors, one can safely suggest that the final angle α_{loc} is about $(58.05 \pm 1.04)^\circ$. Obviously, the lower limit ($\approx 57.01^\circ$) is still larger than that ($\approx 56.65^\circ$) of the host value. The estimated angle α_{loc} in this work remains to be further checked with experiments.

In conclusion, the EPR parameters for $ZnSiP_2$:Fe^+ are satisfactorily interpreted and the local structure of this tetragonal Fe^+ center is also obtained. It appears that useful information about the local structure for an Fe^+ (or other $3d^7$) impurity ion in $ZnSiP_2$ (or other similar II_B-IV-V_2 and I_B-III-IV_2 semiconductors) can be acquired by analyzing its EPR data.

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