Calculation of the EPR Parameters and the Local Structure for Fe⁺ on the Zn²⁺ Site of ZnSiP₂

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Z. Naturforsch. 59a, 769 – 772 (2004); received March 25, 2004

The zero-field splitting $D$, $g$ factors $g_\parallel$ and $g_\perp$ and the local structure near Fe⁺ on the Zn²⁺ site of ZnSiP₂ 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 $\alpha_{\text{loc}}$ related to the fourfold axis is about 58.05° in the studied Fe⁺ impurity center, which is larger than the metal-ligand bonding angle $\alpha_{\text{h}} (\approx 56.65°)$ in pure ZnSiP₂. The EPR parameters based on the above angle $\alpha_{\text{loc}}$ 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⁺; ZnSiP₂.

1. Introduction

ZnSiP₂ belongs to the ternary semiconductors of type II₈-IV-V₂ and I₈-III-IV₂ 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 ZnSiP₂ 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-II₈ (Zn²⁺) and group-IV (Si³⁺) 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 Zn²⁺ ion in ZnSiP₂ were reported, and the EPR parameters zero-field splitting $D$ and $g$ factors $g_\parallel$ 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 ZnSiP₂ may help to understand its optical and electronic properties. In the present work, the local structure and the EPR parameters for Fe⁺ on the Zn²⁺ site of ZnSiP₂ 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
parameters $D_{i}$, $g_{||}$ and $g_{\perp}$ for a 3d$^7$ ion in tetragonally distorted tetrahedra are derived. They are [11]

$$D = (35/9)D_{q}\zeta^{2}/[1/E_{t}^{2} - 1/E_{g}^{2}]$$

$$-35BD_{q}\zeta^{2}/(3E_{t}^{2})$$

$$g_{||} = g_{s} + 8k'\zeta/(3E_{t})$$

$$-2\zeta'/(2k' - k' + 2g_{s}k)/(9E_{t}^{2})$$

$$+4\zeta'^{2}/(k - 2g_{s})(9E_{t}^{2}) - 2\zeta'^{2}/(k + g_{s})(3E_{g}^{2})$$

$$+k'\zeta'[4/(9E_{g}^{3}) - 4/(3E_{g}^{3}) + 4/(3E_{g}^{3})]$$

$$-140k'\zeta'/D_{q}/(9E_{t}^{2})$$

$$g_{\perp} = g_{||} + 210k'\zeta'/D_{q}/(9E_{t}^{2})$$

where $g_{s} (= 2.0023)$ is the spin-only value. The denominators $E_{t}(i = 1 - 3)$ 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 $D_{q}$ and the Racah parameters $B$ and $C$ for the studied system:

$$E_{1} = 10D_{q}$$

$$E_{2} = 15B + 5C$$

$$E_{3} = 10D_{q} + 9B + 3C$$

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

$$\zeta = N_{t}[\zeta_{0}^{0} + (\sqrt{2}\lambda_{\alpha}\lambda_{\sigma} - \lambda_{\alpha}^{2}/2)\zeta_{p}^{0}]$$

$$\zeta' = N_{t}[\zeta_{0}^{0} + (\lambda_{\alpha}\lambda_{\sigma}/\sqrt{2} + \lambda_{\sigma}^{2}/2)\zeta_{p}^{0}]$$

$$k = N_{t}[1 - \lambda_{\sigma}^{2}/2 + \sqrt{2}\lambda_{\alpha}\lambda_{\sigma} + 2\lambda_{\alpha}\lambda_{\sigma}(\sigma) + 2\lambda_{\alpha}\lambda_{\sigma}(\pi)]$$

$$k' = N_{t}[1 + \lambda_{\sigma}^{2}/2 + \lambda_{\alpha}\lambda_{\sigma}/\sqrt{2} + 4\lambda_{\alpha}\lambda_{\sigma}(\pi)]$$

where $\zeta_{0}^{0}$ 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. $\lambda_{\alpha}\lambda_{\sigma}(j = e$ and t, which stand for the irreducible representations of the $T_{d}$ group) are the normalization factors and $\lambda_{j}$ ($j = \sigma$ and $\pi$ are the orbital mixing coefficients. They satisfy the normalization conditions:

$$N_{t} = [1 + \lambda_{\sigma}^{2} + \lambda_{\pi}^{2} + 2\lambda_{\alpha}\lambda_{\sigma}(\pi)]^{1/2}$$

$$N_{e} = [1 + 3\lambda_{\sigma}^{2} + 6\lambda_{\alpha}\lambda_{\sigma}(\pi)]^{1/2}. $$

$D_{i}$ in (1) is the tetragonal field parameter, which can be determined from the superposition model as follows [12]:

$$D_{i} = 4\tilde{A}_{4}(R)[(1 - \cos^{2}\alpha)^{2}$$

$$+ (35\cos^{4}\alpha - 30\cos^{2}\alpha + 3)]/21,$n

where $\tilde{A}_{4}(R)$ is the intrinsic parameter with the reference bonding length (or metal-ligand distance) $R$. For a 3d$^{n}$ ion in tetrahedra we have $\tilde{A}_{4}(R) \approx (27/16)/D_{q}$ [12, 13]. $\alpha$ 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$^{3+}$-P$^{3-}$-cluster were reported, we estimate the parameters $N_{t}$, $N_{e}$ (which are related to the covalency factor $\beta$ by the relationship $N_{t}^{4} \approx N_{e}^{4} \approx \beta \approx B/B_{0} \approx C/C_{0}$ [14, 15]) and $D_{q}$ from the empirical formulas [14, 15]

$$10D_{q} \approx f(L)g(M), \quad 1 - \beta \approx h(L)k(M),$$

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$^{3+}$-P$^{3-}$ cluster, the values $g(Fe^{3+})$ and $k(Fe^{3+})$ 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 $g(Fe^{3+}) \approx 9000$ cm$^{-1}$, $g(Ni^{3+}) \approx 18000$ cm$^{-1}$, $k(Fe^{3+}) \approx 0.24$, $k(Fe^{3+}) \approx 0.49$, 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

$$g(Fe^{3+}) \approx 4500$ cm$^{-1}$, $k(Fe^{3+}) \approx 0.15$$

for Fe$^{3+}$ and

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

for P$^{3-}$. So, the optical spectral parameters $D_{q}$ is 350 cm$^{-1}$ and $\beta \approx 0.55$ can be calculated from (6). These values are comparable with those ($D_{q}$ is 470 cm$^{-1}$ and $\beta \approx 0.43$ [16]) of the isoelectronic Co$^{2+}$-P$^{3-}$ cluster in GaP, where the metal-ligand distance $R$ ($\approx 2.36$ Å [17]) is close to that ($\approx 2.375$ Å [7]) for the Zn$^{2+}$ site in ZnSiP$_{2}$ of this work. This point is also consistent with the tendency that $D_{q}$ decreases and the covalency factor $\beta$ increases with decreasing valence of isoelectronic ions (such as 3d$^{2}$ ions Cr$^{4+}$, V$^{3+}$, Ti$^{2+}$ and 3d$^{3}$ ions Fe$^{3+}$, Mn$^{2+}$) for the same ligands [14, 15]. Therefore, the spectral parameters obtained for the Fe$^{3+}$ center in ZnSiP$_{2}$ of this work can
Table 1. The EPR parameters based on the host and local structural parameters of \( \text{Fe}^+ \) in ZnSiP2.

<table>
<thead>
<tr>
<th></th>
<th>Host</th>
<th>Local</th>
<th>Exp. [8]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cal.(^a)</td>
<td>Cal.(^b)</td>
<td>Cal.(^b)</td>
</tr>
<tr>
<td>( g^\parallel )</td>
<td>2.130</td>
<td>2.126</td>
<td>2.119</td>
</tr>
<tr>
<td>( g^\perp )</td>
<td>2.153</td>
<td>2.150</td>
<td>2.160</td>
</tr>
<tr>
<td>( D ) (in ( \text{cm}^{-1} ))</td>
<td>1.26</td>
<td>1.19</td>
<td>2.25</td>
</tr>
</tbody>
</table>

\(^{a}\) 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 \( \text{Fe}^+ \) [18].

By using the above metal-ligand distance \( R \) (≈ 2.375 Å [7]) and the Slater-type SCF functions [19, 20], the group overlap integrals \( S_{\text{dd}}(\pi) \approx 0.014 \) and \( S_{\text{dd}}(\sigma) \approx -0.036 \) 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 \( \zeta_{\pi} \approx 356 \text{ cm}^{-1} \) [18] for \( \text{Fe}^+ \) and \( \zeta_{\sigma} \approx 299 \text{ cm}^{-1} \) [21] for \( \text{P}^3^- \) 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 \( \alpha_0 \approx 56.65^\circ \) [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 expected values 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 \( \text{Fe}^+ \) may be a result of an effect that is not related to 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 \( \tau_{\text{loc}} \) was found to be different from the host one \( \tau \) [22]. The tetragonal distortion of the studied system (the impurity \( \text{Fe}^+ \) on a group-\( II_B \) Zn\(^{2+}\) site) is related to the angle \( \alpha \), which depends upon the tilting angle \( \tau \) and the atomic position parameter \( x \). These relationships can be expressed as [6]

\[
\cos \alpha \approx \eta (16x^2 + \eta^2 + 1)^{-1/2}
\]  

(9)

and

\[
tg \tau \approx (1 - 4x)/(1 + 4x),
\]  

(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 \( r_{\text{loc}} \approx 0.2957 \) 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 \( \zeta_{\pi} = 0, \lambda_{\pi} = \lambda_{\sigma} \) and \( N_{\pi} = N_{\sigma} = \beta^{1/6} \)) are also collected in Table 1.

3. Discussions

According to the above investigations, the theoretical EPR parameters based on the local tilting angle \( \tau_{\text{loc}} \) for \( \text{Fe}^+ \) on the Zn\(^{2+}\) site in ZnSiP\(_2\) agree better with the observed values than those based on the host angle \( \tau \). 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 \( r_{\text{loc}} \approx 0.2957 \) obtained in this work are different from \( \alpha_0 \approx 56.65^\circ \), \( \tau_0 \approx -2.1^\circ \) and \( r_0 \approx 0.2691 \) obtained in [7]. Since the tetragonal distortion may be characterized by the angular deviation \( \Delta \alpha = \alpha - \alpha_0 \), where \( \alpha_0 \approx 54.74^\circ \) (the corresponding angle for the cubic case), the local tetragonal distortion in the vicinity of the impurity \( \text{Fe}^+ \) is larger than that of the host Zn\(^{2+}\) site due to the larger tilting angle \( \tau_{\text{loc}} \) 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 \( \text{Fe}^+ \) should be larger than that of the replaced Zn\(^{2+}\) and make the local [FeP\(_4\)]\(^{1-}\) cluster tighter. So, the angle \( \alpha \) 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 \( \alpha_{\text{loc}} \) and \( \tau_{\text{loc}} \) for the impurity \( \text{Fe}^+ \) center compared with those for the host can be understood.

2) For \( \text{Fe}^+ \) in ZnSiP\(_2\) of this work, where the covalency is strong (\( \beta \approx 0.55 \approx 1 \)) and the S.O. coupling coefficient (\( \approx 299 \text{ cm}^{-1} \)) of the ligand P\(^3-\) is comparable with that (\( \approx 356 \text{ cm}^{-1} \)) of the central Fe\(^{2+}\) 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 $\tau_{\text{loc}}$ to about $-4.5^\circ$, 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 $\text{Fe}^+$ in $\text{ZnSiP}_2$.

(3) There are some errors in the above calculations. (i) The actual distance between the impurity $\text{Fe}^+$ and the ligand $\text{P}^3^-$ may differ somewhat from that of the metal-ligand distance $R$ in pure $\text{ZnSiP}_2$ due to the difference between the size of the $\text{Fe}^+$ and that of the replaced $\text{Cd}^2^+$. Fortunately, this discrepancy would only affect very slightly the group overlap integrals $S_{dp}(j)$ as well as the parameters $\zeta$, $\zeta'$ etc. in (3). Thus, the errors of the EPR parameters and the angle $\alpha_{\text{loc}}$ are smaller than 0.1%, since the tetragonal distortion of the studied system depends only on the angle $\alpha$ (see (5)), and is almost independent of the distance $R$. (ii) Approximation of the parameters (i.e., $g$ and $k$ for $\text{Fe}^+$ and $f$ and $h$ for $\text{P}^3^-$ in (7) and (8)) and the empirical formulas (6) can bring errors to the value of $Dq$ or $\beta$ 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 $\alpha_{\text{loc}}$ 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 $\alpha_{\text{loc}}$ is about $(58.05 \pm 1.04)^\circ$. Obviously, the lower limit (≈ 57.01°) is still larger than that (≈ 56.65°) of the host value. The estimated angle $\alpha_{\text{loc}}$ in this work remains to be further checked with experiments.

In conclusion, the EPR parameters for $\text{ZnSiP}_2:\text{Fe}^+$ are satisfactorily interpreted and the local structure of this tetragonal $\text{Fe}^+$ center is also obtained. It appears that useful information about the local structure for an $\text{Fe}^+$ (or other 3d$^7$) impurity ion in $\text{ZnSiP}_2$ (or other similar II-VI-IV$_2$ and IB-III-IV$_2$ semiconductors) can be acquired by analyzing its EPR data.