# Zero-field Splitting and Local Lattice Distortions for $Fe^{3+}$ Ions in Some $I_b$-$III_b$-$VI_2$ Semiconductors

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The EPR zero-field splitting $D$ for $Fe^{3+}$ ions in some $I_b$-$III_b$-$VI_2$ semiconductors is calculated with the superposition model. The calculated $D$ values, when using the local rotation angles $\tau(Fe^{3+})$ for $Fe^{3+}$ in $CuGaS_2$ and $AgGaS_2$ crystals, are consistent with the observed values, whereas for $Fe^{3+}$ in $CuAlS_2$ crystal they are not. The calculated results are discussed. The local lattice distortions except the local rotation angles $\tau$ for $Fe^{3+}$ in $CuAlS_2$ are suggested.

*Key words:* Electron Paramagnetic Resonance; Local Lattice Distortion; Superposition Model; $Fe^{3+}$; $CuMS_2$(M = Al, Ga, In); $AgGaS_2$.

## 1. Introduction

$I_b$-$III_b$-$VI_2$ semiconductors have attracted much interest as new optoelectronic, luminescent and solar-cell materials [1 – 3]. These semiconductors are ternary analogues of II-VI binary compounds. Their crystal structure is derived from the zincblende structure by replacing the zinc ions by ions of group $I_b$ and $III_b$ [4]. Each type of metal ion is surrounded by a tetragonally distorted anion tetrahedron. This distortion is related to a clockwise or counter-clockwise rotation of the anion tetrahedron by an angle $\pm\tau_I$ (or $I_{III}$) around the $C_4$ axis. Transition metal and rare-earth impurity ions in these semiconductors may occur at $I_b$ and $III_b$ sites. Since these impurities can strongly influence the optical and electric properties of these semiconductors, many spectroscopy methods have been applied to study these impurity centers. For example, the EPR spectra of the $Fe^{3+}$ ion, one of the major trace impurities, on the trivalent ($III_b$) metal sites in $CuAlS_2$, $CuGaS_2$, $CuInS_2$ and $AgGaS_2$ were measured, and the zero-field splittings $D$ for $Fe^{3+}$ in these crystal were determined [5, 6]. By analyzing the magnetic site splitting of $Fe^{3+}$-singals in EPR spectra, the local rotation angle $\tau(Fe^{3+})$ of the anion tetrahedron surrounding the $Fe^{3+}$ ion in $CuAlS_2$, $CuGaS_2$, and $AgGaS_2$ was also determined [5, 6]. The local angle $\tau(Fe^{3+})$ in these $Fe^{3+}$-doped crystals is quite different from the corresponding angle $\tau(Me^{3+})$ in the pure (or host) crystal [6] (see Table 1). No theoretical studies for these zero-field splittings $D$ (particularly the unusually large value of $D$ for $Fe^{3+}$ in $AgGaS_2$, the sulfur arrangement around the trivalent cation in pure $AgGaS_2$ being almost an ideal tetrahedron) were made until now. In addition, the other local lattice distortions, except the local rotation angle for these $Fe^{3+}$ centers, were not studied by means of EPR spectra. Since the zero-field splitting of a paramagnetic ion in crystals is sensitive to its immediate environment, in this paper we study the zero-field splitting and the local lattice distortions for $Fe^{3+}$ centers in $I_b$-$III_b$-$VI_2$ semiconductors by the superposition model [7].

## 2. Calculations

The superposition model [7] is a powerful tool in explaining zero-field splitting of $3d^5$ ions and in gaining useful information on the local geometry of these ions in crystals [8 – 10]. From the model, the zero-field splitting $D$ for a $3d^5$ ion in a tetragonally distorted tetrahedron can be written as [7]

$$D = 2\bar{b}_2(R)(3\cos^2\theta - 1), \tag{1}$$

where $\theta$ is the angle between the impurity-ligand

Table 1. The host and local structural data and the intrinsic parameter $\bar{b}_2(R)$ for $Fe^{3+}$ in $I_b$-$III_b$-$VI_2$ semiconductors.

| | $CuAlS_2$ | $CuGaS_2$ | $CuInS_2$ | $AgGaS_2$ |
|---|---|---|---|---|
| $\tau(Me^{3+})$ [6] | 2.1(4)° | 2.6(6)° | –3.8(7)° | 6.9(6)° |
| $\tau(Fe^{3+})$[a] [6] | –5.1(1)° | –5.15(10)° | | –10.9(2)° |
| $R_H$ (Å) [6] | 2.239(10) | 2.235(15) | 2.517(20) | 2.235(15) |
| $R$ (Å) | 2.304(10) | 2.245(15) | 2.432(20) | 2.245(15) |
| $\eta$ [6] | 0.979 | 0.979 | 1.007 | 0.895 |
| $\theta$ (host) [6] | 54.35 (15) | 54.10 (25) | 56.45 (30) | 54.85 (25) |
| $\theta$ (loc.) | 57.87 (5) | 58.06 (6) | | 63.35 (12) |
| $\bar{b}_2(R)$ ($cm^{-1}$) | –0.50(2) | –0.58(2) | –0.36(2) | –0.58(2) |

[a] The sign of $\tau$ ($Fe^{3+}$) was not given in [6].

bonding length $R$ and the $C_4$ axis. $\bar{b}_2(R)$ is an intrinsic parameter which depends the distance $R$ by the power-law $\bar{b}_2 \propto R^{-t_2}$ [7]. For the $Fe^{3+}$ ion, $t_2 \approx 7 \pm 1$ [8]. According to [11], we have

$$\bar{b}_2(R) \approx -\frac{16}{9} G_{11}, \tag{2}$$

where $G_{11}$ is the spin-lattice coupling coefficient for a $3d^5$ ion in a regular tetrahedron [11]. For the $Fe^{3+}$-$S^{2-}$ combination, from the uniaxial dependence of EPR spectra of ZnS:$Fe^{3+}$ [12], one can obtain $G_{11} \approx -0.93(1)\ cm^{-1}$. Thus, we have

$$\bar{b}_2(R) \approx -0.52(1)\ cm^{-1}, \tag{3}$$

where $R$ is the impurity-ligand distance in the ZnS:$Fe^{3+}$ crystal. Generally, $R$ in doped crystals is different from the corresponding metal-ligand distance $R_H$ in the host (or pure) crystal and can be approximately estimated by the formula [13]

$$R = R_H + (r_i - r_h)/2, \tag{4}$$

where $r_i$ and $r_h$ are the ionic radii of the impurity and the replaced host ion, respectively. For ZnS:$Fe^{3+}$, $R_H \approx 2.342$ Å [14], $r_i(Fe^{3+}) \approx 0.64$ Å and $r_h(Zn^{2+}) \approx 0.74$ Å [14], thus $R \approx 2.292$ Å. For $CuAlS_2$, $CuGaS_2$, $CuInS_2$, and $AgGaS_2$ crystals, $r_h(Al^{3+}) \approx 0.51$ Å, $r_h(Ga^{3+}) \approx 0.62$ Å and $r_h(In^{3+}) \approx 0.81$ Å. Thus from (4) the distance $R$ for $Fe^{3+}$ in these crystals can be obtained as collected in Table 1. From the above power-law, $\bar{b}_2(R)$ for $Fe^{3+}$ in these crystals can be estimated and is also shown in Table 1.

The angle $\theta$ in $I_b$-$III_b$-$VI_2$ semiconductors can be calculated by the equation

$$\cos\theta = \frac{\eta}{\sqrt{16(x-\frac{1}{2})+1+\eta^2}}, \tag{5}$$

Table 2. The zero-field splittings $D$ (in $10^{-4}\ cm^{-1}$) for $Fe^{3+}$ ions in $I_b$-$III_b$-$VI_2$ semiconductors.

| | $CuAlS_2$ | $CuGaS_2$ | $CuInS_2$ | $AgGaS_2$ |
|---|---|---|---|---|
| Cal.[a] | −190(80) | −365(140) | 600(140) | 65(150) |
| Cal.[b] | 1510(150) | 1860(100) | | 4600(200) |
| Cal.[c] | 920(60) | | | |
| Expt. [5, 6] | 900(1) | 1886(1) | 990(2) | 4871(2) |

[a] Calculated from the host values of $\tau(Me^{3+})$ and $\eta$. [b] Calculated from the host value of $\eta$ and the local value of $\tau(Fe^{3+})$. [c] Calculated from the local values of $\tau$ ($Fe^{3+}$) and $\eta$.

where $\eta = \frac{c}{2a}$ ($a$ and $c$ are the lattice constants, the $\eta$ values for the four $I_b$-$III_b$-$VI_2$ semiconductors are collected in Table 1). $x$ is the atomic position parameter which is related to the rotation angle $\tau$ by the formula [5]

$$x = \frac{3tg\tau + 1}{4(1 + tg\tau)}. \tag{6}$$

Thus, from the rotation angle $\tau$ and the value of $\eta$, the angle $\theta$ and hence the zero-field splitting $D$ for $Fe^{3+}$ in the above semiconductors can be calculated. The calculated angels $\theta$ are shown in Table 1, and the calculated values of splitting $D$ by using the local rotation angel $\tau(Fe^{3+})$ and those by using the corresponding angle $\tau(Me^{3+})$ in pure crystals are compared with the observed values in Table 2.

## 3. Discussion

1. From Table 2, it can be found that for $Fe^{3+}$ in $CuGaS_2$ and $AgGaS_2$, the calculated splitting $D$ using the host value of $\eta$ and the local value of $\tau(Fe^{3+})$ is consistent with the observed value, whereas the calculated $D$ using the host $\tau(Me^{3+})$ disagrees with the observed value. Considering that the ionic radii of the impurity $Fe^{3+}$ ($r_i \approx 0.64$ Å [14]) and the replaced host ion $Ga^{3+}$ ($r_h \approx 0.62$ Å [14]) are very close to each other, the other local lattice distortions related to the bonding length $R$ (see Table 1) and the value of $\eta$ can be regarded as very small. So, the above calculated results using the local $\tau(Fe^{3+})$ and host $\eta$ can be viewed as suitable and the zero-field splittings $D$ for the $Fe^{3+}$ in $CuGaS_2$ and $AgGaS_2$ are explained reasonably. The unusually large zero-field splitting $D$ for $AgGaS_2$:$Fe^{3+}$ occurs because the local rotation angle $\tau(Fe^{3+})$ is opposite in sign and larger in magnitude than the corresponding host angle $\tau(Me^{3+})$, and so it results in a very large tetragonal distortion of the anion tetrahedron (note: the tetragonal distortion can be characterized by

$|\Delta\theta| = \theta - \theta_0$, where $\theta_0 \approx 54.74°$, the angle in a regular tetrahedron). In passing, the tetragonal distortion of the anion tetrahedron in the host $AgGaS_2$ is indeed very small (see Table 1), and so the calculated splitting $D$ using the host value, is also very small (see Table 2).

2. For $CuAlS_2:Fe^{3+}$, however, the calculated splitting $D$, by using the local $\tau(Fe^{3+})$ and the host $\eta$ agrees poorly with the observed value (see Table 2). It is astonishing that the host values of $\eta$, $R_H$, $\tau(Me^{3+})$ and the local value of $\tau(Fe^{3+})$ for $CuAlS_2:Fe^{3+}$ are close to those for $CuGaS_2:Fe^{3+}$ (see Table 1), but the experimental value of $D$ in $CuAlS_2:Fe^{3+}$ is only half of that in $CuGaS_2:Fe^{3+}$. The reasons, in our opinion, may be because in $CuAlS_2:Fe^{3+}$ the ionic radius ($\approx 0.64$ Å [14]) of the impurity $Fe^{3+}$ is much larger than that ($\approx 0.51$ Å [14]) of the replaced host ion $Al^{3+}$. So, we suggest that not only the local rotation angle $\tau(Fe^{3+})$, but also the local values of $R$ (see Table 1) and $\eta$ are different from the corresponding host values in $CuAlS_2:Fe^{3+}$ crystal. If we change $\eta$ from 0.979 to 1.025, the calculated $D$ value is consistent with the observed value (see Table 2). So, we suggest the local value $\eta \approx 1.025$ for $CuAlS_2:Fe^{3+}$.

3. For $CuInS_2:Fe^{3+}$ the magnetic site splitting of the $Fe^{3+}$-singals could not be resolved, and so the local rotation angle $\tau(Fe^{3+})$ could not be determined because of the large inhomogeneous broadening of the EPR lines, resulting from the nuclear moments of the $In^{115}$ ligand [6]. So, the calculated splitting $D$, using the local $\tau(Fe^{3+})$, can not be given. Interestingly, the calculated splitting $D$ using the host values of $\tau(Me^{3+})$ and $\eta$ is close to the observed value (see Table 2). However, since the impurity $Fe^{3+}$ is smaller than ($\approx$ 0.81 Å) the host $In^{3+}$, we presume that the local values of $\tau(Fe^{3+})$ and $\eta$ are slightly different from the corresponding host values. This point remains to be further studied.

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