Spectroscopic analysis of erbium-doped silicon and ytterbium-doped indium phosphide

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Chapter 4

Zeeman splitting factor of the Er$^{3+}$ ion in a crystal field

4.1 Introduction

Magnetic resonance has provided valuable knowledge on the atomic and electronic structure of rare-earth impurities in crystalline hosts, such as in elemental and compound semiconductors. The spectroscopic information as obtained by recording angular dependence on magnetic field is commonly analysed in the spin-Hamiltonian formalism. In the Hamiltonian as typically required, $\mathcal{H} = \mu_B \mathbf{B} \cdot \mathbf{J} + J \cdot \mathbf{A} \cdot \mathbf{I}$, the first term represents the Zeeman energy of the spin $\mathbf{J}$ in the magnetic field $\mathbf{B}$, whereas the second term gives the hyperfine interaction energy with isotopes of nuclear spin $\mathbf{I}$. By analysing the experimental data the Zeeman splitting or $g$ tensor and the hyperfine interaction tensor $\mathbf{A}$, which commonly serve as a unique characterisation of the spectrum, are determined.

For the case of erbium, the isotope $^{167}$Er has the non-zero spin $I = 7/2$ and is present with the natural abundance of 23%. For erbium, therefore, the structure of eight hyperfine satellite lines, is expected, to first order displaced symmetrically with respect to the central line of the $I = 0$ isotopes, and with an intensity of 3.7% of the central line. Observation of such hyperfine structure in the electron paramagnetic resonance (EPR) spectrum allows unambiguous identification of the impurity. Unfortunately, due to low abundance of the isotope the weak hyperfine lines are not always observable.

For instance, this has been the case for recently described erbium centres in silicon [4.1, 4.2]. In this case the identification in magnetic resonance must rely on the fine structure tensor $g$ of the Zeeman splitting. In order to assess the effect of a magnetic field on the paramagnetic rare-earth ion its electronic state as created by the stronger perturbations, i.e., firstly the spin–orbit interaction and, secondly, the crystal field, must be well known.
The subject of this chapter is the derivation of the $g$ tensor of erbium centres in crystal fields of various symmetries. Energies of states are calculated with and without a magnetic field applied. Due to the high value of the electron spin and the complexity of the interactions, exact analytical solutions are restricted to some special cases only. Therefore, the calculations were carried out fully numerically. Reference is made to analytical solutions based on exact treatment or approximate perturbation methods when available.

Over the last 40 years the EPR spectrum of the erbium ion, as an isolated impurity, in several crystals has been reported [4.1 - 4.37]. In the experiments the energy difference between Zeeman levels is measured and the $g$ value is calculated as a positive number from the resonance condition $h\nu = g\mu_B B$, with $h\nu$ the microwave quantum. Only in an exceptional case the sign of $g$ values was determined in a dedicated experimental set-up [4.36]. Following this practice the principal spectroscopic parameters from experiment are given in table 4.1 as positive. The $g$ tensor data for isotropic and axial centres are as well represented in figure 4.1.

![Figure 4.1](image_url)

**Figure 4.1** Plot of values $g_\perp$ versus $g_\parallel$ for magnetic resonance spectra of axial and isotropic $\text{Er}^{3+}$ centres in several crystalline hosts corresponding to the data as given in table 4.1. The lines surrounding the shaded area represent tensors with traces $g_\parallel + 2g_\perp = 18.0$ and 20.4; in the isotropic case $g_\parallel = g_\perp = 6$ for $\Gamma_6$ states and $g_\parallel = g_\perp = 6.8$ for $\Gamma_7$ states.
Table 4.1 Principal $g$ values of $\text{Er}^{3+}$ spectra in various semiconductor, and some insulator, host crystals.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Host</th>
<th>$g$ values</th>
<th>Reference</th>
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<td>4.03</td>
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</tbody>
</table>

1. LaES = La(C$_2$H$_5$SO$_4$)$_3$·9H$_2$O
2. YES = Y(C$_2$H$_5$SO$_4$)$_3$·9H$_2$O

4.2 Method of calculation

4.2.1 Spin–orbit interaction

For rare-earth ions the magnetic properties are dictated by the electrons in the incompletely filled 4f shell. For Er$^{3+}$ with the configuration 4f$^{11}$ the orbital momentum is $L = 6$ and the electron spin is $S = 3/2$. By the spin–orbit interaction $\lambda L \cdot S$ these states group into four levels with total angular momentum $J = L + S = 15/2$, $J = 13/2$, $J = 11/2$ and $J = L - S = 9/2$, respectively. As for the Er$^{3+}$ ion the spin–orbit constant $\lambda$ is negative, the state $J = 15/2$ forms the ground state. It is separated from the next higher state, with $J = 13/2$, by about 800 meV. Calculations are restricted to the isolated ground state with 16-fold degeneracy. In the spin $J$ formalism the Landé factor for splitting in a magnetic field is $g_J = 1 + [J(J+1) - L(L+1) + S(S+1)]/2J(J+1) = 6/5$.

4.2.2 Crystal field

Incorporated in a crystal the erbium ion is subject to the fields exerted by surrounding host atoms. In the crystal field the 16-fold degeneracy of the $J = 15/2$ spin–orbit level is lifted, the precise effect depending on strength and symmetry of the crystal field. For a high-
symmetry cubic surrounding the splitting will be into three quartets and two doublets; for a low-symmetry field the maximum number of eight Kramers doublets will be obtained. Calculations of the energy levels were performed for centres of cubic, trigonal, tetragonal and orthorhombic symmetry. The crystal potentials are represented by their corresponding spin operators $H_{cf}$. Crystal-field induced splittings are of order of magnitude 50 meV.

4.2.3 Magnetic field

The Zeeman splitting of about 0.1 meV induced in an EPR experiment in the K band (frequency 23 GHz) is only a small perturbation on the states formed after spin–orbit and crystal-field interactions. Energies of the $J = 15/2$ spin–orbit ground state sublevels are calculated in the presence of a crystal field and a magnetic field. The energy of the Zeeman effect is calculated by applying the operator $H_{mf} = g \mu_B B \cdot J$. By the magnetic field the degeneracy in the crystal-field quartet and doublet levels is lifted. By taking a reasonable weak magnetic field the effective $g$ values are directly obtained as the energy differences between levels. For example, in case of low symmetry $g_i = E_{i+} - E_{i-}$, $i = 1,\ldots,8$. Calculations are restricted to the low-field regime with linear Zeeman splitting and consequently constant $g$ values by proper scaling of the crystal-field coefficients. To match existing conditions in the total spin Hamiltonian $H = H_{cf} + H_{mf}$ the magnetic field was chosen so that the relation of the parameter $V_{cf}$ included in the expression for $H_{cf}$ and $\mu_B$ is like 1000 : 1. The variation of this parameter $V_{cf}$ over a wide range did have no effect on calculated $g$ values. However, the computational scheme, in which only energies of states are calculated, is of a general nature and allows larger fields to be applied and non-linear effects to be calculated without modification. Calculations have included centres from high cubic symmetry with isotropic EPR spectra and scalar $g$ values, centres of trigonal and tetragonal symmetry with axial tensors with principal values $g_\| $ and $g_\perp$, and centres of the lower orthorhombic or monoclinic symmetry with three independent principal $g$ values $g_1$, $g_2$ and $g_3$.

4.3 Cubic symmetry

4.3.1 Energy

In case of cubic symmetry and $f$ electrons the possible crystal field operators are of fourth and sixth order in spin $J$. The former operator is specified by
\[ H_{cu4} = O_4^0 + 5O_4^4, \quad (4.1a) \]

with

\[ O_4^0 = 35J_z^4 - [30J(J + 1) - 25]J_z^2 - 6J(J + 1) + 3J^2(J + 1)^2 \quad (4.1b) \]

and

\[ O_4^4 = \frac{1}{2}(J_z^4 + J_z^2) \quad (4.1c) \]

The operator of sixth order is given by

\[ H_{\infty} = O_6^0 - 21O_6^4, \quad (4.2a) \]

with

\[ O_6^0 = 231J_z^6 - 105[3J(J + 1) - 7]J_z^4 + 105J^2(J + 1)^2 - 525J(J + 1)^2 + 294J^2(J + 1)^2 -
\]
\[ - 5J^3(J + 1)^3 + 40J^2(J + 1)^2 - 60J(J + 1) \quad (4.2b) \]

and

\[ O_6^4 = \frac{1}{4}[11J_z^2 - 7J(J + 1) - 38][J_z^4 + J_z^2] + \frac{1}{4}[J_z^4 + J_z^2][11J_z^2 - J(J + 1) - 38]. \quad (4.2c) \]

The linear combination

\[ H_{ct} = V_{ct}H_{cu} \quad (4.3a) \]

with

\[ H_{cu} = \sin \alpha H_{cu4}/ F(4) + \cos \alpha H_{cu6}/ F(6) \quad (4.3b) \]

involving the two parameters \( V_{ct} \) and \( \alpha \), with \( \alpha \) in the range \(-90^\circ \leq \alpha \leq +90^\circ\), represents the general case. To obtain more convenient values of parameters it is customary to introduce the dividers \( F(4) = 60 \) and \( F(6) = 13860 \) in the expression \( (4.3b) \) [4.39 - 4.41]. Energy
eigenvalues $E$ of the Hamiltonian (4.3a, b) for $V_{cf} = +1$ in the basis set of 16 states $m_l = -15/2$ to $+15/2$ are given in figure 4.2. For the doublet $\Gamma_6$ the exact result is $E = V_{cf}(-40\cos\alpha + 294\sin\alpha)$, for the $\Gamma_7$ doublet $E = V_{cf}(-312\cos\alpha - 26\sin\alpha)$. Energies of the quartet states ($\Gamma_8)_i$, $i = 1, 2$ and 3, are the numerically computed solutions of cubic equations. Except for the different choice of parameters the result is identical to the classical data of Lea, Leask and Wolf [4.40]. The two parameter sets are related by $V_{cf}\sin\alpha = Wx$ and $V_{cf}\cos\alpha = W(1-|x|)$.

On the basis of a point charge model a positive value of $V_{cf}$ is expected. If so, inspection of figure 4.2 shows that the ground state will be of doublet $\Gamma_6$ character for $-90^\circ \leq \alpha \leq -40.4^\circ$, of character $\Gamma_7$ for $-40.4^\circ \leq \alpha \leq +54.5^\circ$ and ($\Gamma_8)_1$ for $+54.5^\circ \leq \alpha \leq +90^\circ$. For a substitutional site of erbium, with a fourfold co-ordination of ligands, the parameter $\alpha$ will be negative and the ground state will be the $\Gamma_6$ or $\Gamma_7$ doublet. On an interstitial site, with octahedrally coordinated neighbours and positive $\alpha$, ground states of $\Gamma_7$ or ($\Gamma_8)_1$ character are possible.

![Figure 4.2 Crystal-field energies of doublets $\Gamma_6$ and $\Gamma_7$ and of quartets ($\Gamma_8)_i$, $i = 1, 2$ and 3, in the cubic case representing the eigenvalues of equation (4.3) with $V_{cf} = +1$. Parameter $\alpha$, in the range $-90^\circ \leq \alpha \leq +90^\circ$, controls the mixing of the fourth- and sixth-order cubic crystal fields.](image)
4.3.2 g Value

Splitting of the doublet states in a magnetic field can be described by an effective spin \(1/2\) and labelling of the states as \(|\pm>\). In the cubic field the conjugate wave functions of the doublets are expressed in the basis states \(|m_i>\) of the \(J = 15/2\) level by \(\Sigma c_j|m_j>\). For \(\Gamma_7\) one obtains, independent of parameter \(\alpha\),

\[|\Gamma_7\rangle = \frac{1}{24}\sqrt{33}\left|\pm \frac{11}{2}\right> + \frac{1}{8}\sqrt{13}\left|\pm \frac{3}{2}\right> - \frac{1}{24}\sqrt{195}\left|\pm \frac{5}{2}\right> - \frac{1}{24}\sqrt{231}\left|\pm \frac{13}{2}\right>\]  

(4.4)

The splitting is isotropic with the effective \(g\) factor given by \(g = 2\omega\Sigma c_j^2m_j = 34/5\). In an equivalent way the wave functions for \(\Gamma_6\) are:

\[|\Gamma_6\rangle = \frac{1}{24}\sqrt{195}\left|\pm \frac{15}{2}\right> + \frac{1}{8}\sqrt{7}\left|\pm \frac{7}{2}\right> + \frac{1}{8}\sqrt{33}\left|\pm \frac{1}{2}\right> + \frac{1}{24}\sqrt{21}\left|\pm \frac{9}{2}\right>\]  

(4.5)

and the isotropic effective \(g\) value is \(g = 6\).

From the values listed in table 4.1 for the semiconductors GaAs, ZnS, ZnSe, ZnTe and CdTe the experimental values close to 6 indicate a \(\Gamma_6\) ground state and the negative value of \(\alpha\) confirms a substitutional erbium position. In contrast, for erbium in CaF\(_2\), CdF\(_2\), CeO\(_2\) and ThO\(_2\) a \(\Gamma_7\) ground state is indicated by their \(g\) value. The small negative deviations of experimental values from the calculated numbers, discussed in several papers, have been ascribed to admixture of the higher terms \(^2K_{15/2}\) and \(^2L_{15/2}\), admixture of \(\Gamma_8\) state by the magnetic field and covalent delocalization [4.12, 4.21, 4.22, 4.27, 4.42]. It may be concluded that the theoretical description provides good agreement with experimental data. However, a precise value of parameter \(\alpha\) cannot be derived. For quartet states \(\Gamma_8\) the splitting of the four levels in a magnetic field can be described by effective spin \(J = 3/2\) and the cubic spin Hamiltonian

\[H = g\mu_B\mathbf{B}\cdot\mathbf{J} + u\mu_B\mathbf{B}\cdot\mathbf{J}^3 = g\mu_B\mathbf{B}\cdot\mathbf{J} + u\mu_B(B_xJ_x^3 + B_yJ_y^3 + B_zJ_z^3).\]  

(4.6)

Numerically calculated values for \(g\) and \(u\) for the three quartet levels are given in figure 4.3. It can be observed that in the crystal field the coefficient \(u\) of the cubic operator is not always small compared to the \(g\) value of the magnetic-dipole Zeeman effect. For this reason the angular dependence following the function (4.7) breaks down [4.22, 4.41, 4.43, 4.44]

\[p(\theta) = 1 - 5\sin^2\theta + 3.75\sin^4\theta.\]  

(4.7)
Figure 4.3 g Values of doublet and quartet levels in cubic symmetry pertaining to the Hamiltonian given in equation (4.6). Parameter $\alpha$, in the range $-90^\circ \leq \alpha \leq +90^\circ$, controls the mixing of the fourth- and sixth-order contributions.

4.4 Trigonal and tetragonal symmetry

4.4.1 Energy

As can be noted in table 4.1 several erbium-related centres were found to have axial symmetry. Their symmetry was either established as trigonal, with axis along a $<111>$ direction, tetragonal, with axis along $<100>$, or the axis was left unspecified. In the trigonal case the leading crystal-field operator of second order is given by
\[
H_w = -\frac{\sqrt{3}}{4}iJ_z^2 + \frac{\sqrt{3}}{4}iJ_z^2 + \frac{\sqrt{3}}{4}(1-i)J_zJ_z + \frac{\sqrt{3}}{4}(1-i)J_zJ_z + \frac{\sqrt{3}}{4}(1+i)J_zJ_z
\]

in the Cartesian coordinate system. Including a cubic contribution as well, the general crystal-field operator will be expressed by

\[
H_{cf} = V_{cf}H_{cutr},
\]

(4.9a)

with

\[
H_{cutr} = \cos\beta H_{cu} + \sin\beta H_{tr}/F(2),
\]

(4.9b)

and with parameter \( \beta \), in the range \(-90^\circ \leq \beta \leq +90^\circ \), specifying the cubic and trigonal components. A factor \( F(2) = 0.1 \) is included in the trigonal field term to obtain better match of the two contributions in the \( J = 15/2 \) spin system. In the trigonal field all orbital degeneracy is removed and the spectrum will consist of eight doublet levels. For two selected cases of parameter \( \alpha \), \( \alpha = -90^\circ \) and \( \alpha = +30^\circ \), the energy eigenvalues of \( H_{cutr} \) are shown in figures 4.4(a) and 4.4(b). Treating the case of tetragonal field in the similar way, the pertinent second-order crystal-field operator is

\[
H_w = J_z^2 - \frac{1}{3}J(J+1).
\]

(4.10)

Combined with a cubic field the total crystal-field operator will be

\[
H_{cf} = V_{cf}H_{cutr},
\]

(4.11a)

with

\[
H_{cutr} = \cos\beta H_{cu} + \sin\beta H_{tr}/F(2),
\]

(4.11b)

again with \(-90^\circ \leq \beta \leq +90^\circ \). Energies of eight doublets as a function of \( \beta \) computed with \( V_{cf} = +1 \) for two values of \( \alpha \), \( \alpha = -90^\circ \) and \( \alpha = +30^\circ \), are given in figures 4.4(c) and 4.4(d). For the limiting values \( \beta = \pm 90^\circ \) only the axial trigonal or tetragonal field is present. In this field the states quantize as \( \mid 15/2, \pm m \rangle \), with quantization axis taken along the axial direction. The corresponding energies of \( H_{cutr} \) and \( H_{cute} \) are \( \pm 210, \pm 190, \pm 150, \pm 90, \pm 10, \pm 90, \pm 210 \) and

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Figure 4.4 Energies of eight doublets for fourth- or sixth-order cubic crystal field together with a second-order trigonal or tetragonal crystal field, calculated from Equations (4.9) or (4.11) with $V_{cf} = +1$ for (a) $\alpha = -90^\circ$, trigonal, (b) $\alpha = +30^\circ$, trigonal, (c) $\alpha = -90^\circ$, etragonal, (d) $\alpha = +30^\circ$, tetragonal. Parameter $\beta$, in the range $-90^\circ \leq \beta \leq +90^\circ$, controls the mixing of the cubic and axial crystal fields.
± 350, in a way as can be verified in the figures 4.4. For $V_{ef} = +1$, as used to draw figures 4.4, the lowest level forms the ground state in which magnetic resonance is observed. For negative $V_{ef}$ the roles of highest and lowest level interchange.

Inspection of figures 4.2 and 4.4 reveals that the ground state can have $\Gamma_6$, $\Gamma_7$ or $\Gamma_8$ symmetry type in cubic field, and be of $m_I = \pm 1/2$ or $\pm 15/2$ character in the pure axial situation. It might be remarked here that among states $|15/2, \pm m_I\rangle$ only the doublet $|15/2, \pm 1/2\rangle$ will give an observable magnetic resonance transition. All other doublets have $g_\perp = 0$, preventing the observation of spin resonance.

### 4.4.2 $g$ Value

Splitting of the spin doublet levels in a magnetic field is expressed by their Zeeman splitting or $g$ factors. Effective $g$ values for the parallel and perpendicular directions in trigonal and tetragonal symmetry were computed by diagonalization of the $16 \times 16$ matrices of the operator $H_{cf} + H_{mf}$ as a function of the parameters $\alpha$ and $\beta$. In the computations as actually carried out parameter $\beta$ was varied in the range $-90$ to $+90$ degrees in steps of 0.1 degree, for values of $\alpha$ spanning the same range in steps of 10 degrees.

Reviewing the results and observing the complex behaviour of $g$ tensor variations one must conclude that a comprehensive and quantitatively accurate analytical treatment of Zeeman effects for a spin system $J = 15/2$ in crystal fields is beyond feasibility. To allow a direct comparison with experimental data as presented in figure 4.1, in the figures 4.5 the calculated perpendicular $g$ value $g_\perp$ is plotted as a function of the calculated parallel value $g_{||}$ for the same $\beta$. In an additional presentation of results, figures 4.6 show the $g_{||}$ and $g_\perp$ values in their dependence on parameter $\beta$.

In the figures 4.4, 4.5 and 4.6 the panels (a) correspond to trigonal centres with $\alpha = -90^\circ$, (b) trigonal, $\alpha = +30^\circ$, (c) tetragonal, $\alpha = -90^\circ$, and (d) tetragonal, $\alpha = +30^\circ$, selected for optimal illustration of the vast amount of data points and the systematics in their behaviour. In cases (a) and (c), for $\beta = 0$ the ground state is $\Gamma_6$ and the isotropic $g$ value $g = 6$ is reproduced. For cases (b) and (d) the ground state is $\Gamma_7$ with $g = 6.8$.

It was shown by Lewis and Sabisky [4.42] that for small axial perturbations the trace $g_{||} + 2 g_\perp$ of the $g$ tensors will stay constant. Inspection of figures 4.5 or 4.6 shows that the theoretical result is unambiguously confirmed for both $\Gamma_6$ and $\Gamma_7$ doublets, both upon trigonal or tetragonal distortion with small $\beta$, and irrespective of parameter $\alpha$ characterising the cubic field. Not shown in the figures, the rule holds equally well if the levels do not form the ground state. Considering next the range of the large axial distortions, for $\beta = +90^\circ$ and $V_{ef} > 0$ the

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Figure 4.5 Plot of $g_\perp$ versus $g_\parallel$ calculated for lowest-energy doublets for (a) $\alpha = -90^\circ$, trigonal, (b) $\alpha = +30^\circ$, trigonal, (c) $\alpha = -90^\circ$, tetragonal, (d) $\alpha = +30^\circ$, tetragonal.
ground state in the purely axial field is $|15/2, m_j = \pm 1/2>$. Exact $g$ values for this state are derived as $g_\parallel = 1.2$ and $|g_\perp| = 9.6$. From figure 4.6(b) for $\alpha = +30^\circ$ it is concluded that $g_\parallel$ and $g_\perp$ have the same sign, hence at $\beta = +90^\circ$ the trace $g_\parallel + 2g_\perp = 20.4$, equal to the trace at the isotropic point $\beta = 0^\circ$.

For $\alpha = -90^\circ$, figure 4.6(a) shows $g_\parallel$ to change sign in the range from $\beta = 0^\circ$ to $\beta = +90^\circ$, around $\beta = 47^\circ$. Assuming $g_\parallel = +1.2$ at $\beta = +90^\circ$, equal to the Landé factor $g = 6/5$, it must be concluded that $g_\perp$ at $\beta = +90^\circ$ has the negative value $g_\perp = -9.6$.

As the sign escapes detection, the measured trace $g_\parallel + 2g_\perp = 20.4$ would easily lead to the erroneous conclusion that the state is $\Gamma_7$ related. At $\beta = 0^\circ$. for the $\Gamma_6$ state in cubic symmetry, the $g$ value must be $g = -6$, but, again, as the sign is not determined in the standard experiment the commonly reported value is positive. The corresponding traces are equal at both $\beta$ points at $-18$.

Also for tetragonal symmetry, as demonstrated by the figures 4.5(c), 4.5(d), 4.6(c) and 4.6(d), the trace at $\beta = +90^\circ$ is exactly equal to its value at $\beta = 0^\circ$. In the region in between a reduction is calculated, but in several cases the trace remains remarkably constant. This is especially true for the case illustrated by figures 4.5(c) and 4.6(c). For this lowest level in tetragonal symmetry and fourth-order cubic field, $\alpha = -90^\circ$, the trace in the whole range for $\beta$ never falls more than $0.3\%$ below the value 18 for the $\Gamma_6$ state. In no case a calculated trace exceeds the value 20.4.

The great majority of the experimental tensors, shown in figure 4.1 in the upper left part, have their trace values slightly below the line $g_\parallel + 2g_\perp = 20.4$. These data are well fitted by the computed curves as shown in figures 4.5(b) and 4.6(b) for trigonal and 4.5(d) or 4.6(d) for tetragonal centres.

It can be concluded that the calculations can well account for the observed $g$ values, thus confirming that they are properly interpreted as due to the $J = 15/2$ spin system of erbium ions. In the results as illustrated in figures 4.5 and 4.6 agreement is reached for $\alpha = +30^\circ$ and $\beta$ values near $+20^\circ$. It must, however, be emphasised that very similar calculated results and consequently similar agreement is achieved for parameter $\alpha$ in the range $-30$ to $+50^\circ$ in which the $\Gamma_7$ level is ground state in cubic symmetry. The data as given above for good agreement are therefore not unique. Just as for the cubic centres, a precise value of $\alpha$ cannot be determined by the analysis. Good fits, though not as convincing and systematic, can also be found in completely different ranges of parameters, e.g., for negative value of $V_{cf}$.

Unfortunately this ambiguity, related to the complexity of interactions, does not allow the above solutions to be presented as unique. In figure 4.1 also a few data points are included for which $g_\parallel > g_\perp$.

An illustration of their matching by the crystal field calculation is given in figure 4.7, which
Figure 4.6 g Values of lowest-energy doublet states including $g_\parallel (- - -)$, $g_\perp (---)$ and trace $g_{tr}$ + $2g_\perp$ (solid line) as a function of parameter $\beta$ for (a) $\alpha = -90^\circ$, trigonal, (b) $\alpha = +30^\circ$, trigonal, (c) $\alpha = -90^\circ$, tetragonal, (d) $\alpha = +30^\circ$, tetragonal. Parameter $\beta$, in the range $-90^\circ \leq \beta \leq +90^\circ$, controls the mixing of the cubic and axial crystal fields.
shows the $g_{\parallel} - g_{\perp}$ relation for the lowest level in tetragonal symmetry for $\alpha = +80^\circ$.

At the same time this figure shows alternative interpretations of the data points in the upper-left corner of the plot, underlining the necessity of care in conclusively selecting matching parameters.

In summary, all experimental data points can be accounted for in the calculations, with exception of the tensors OEr-2 and OEr-2' for centres in silicon [4.1]. Their identification as erbium related is therefore not supported by the present analysis.

Figure 4.7 Plot of $g_{\perp}$ versus $g_{\parallel}$ calculated for lowest-energy doublet in tetragonal symmetry for parameter $\alpha = +80^\circ$. The diamonds indicates the experimental data points for tetragonal centres.
4.5 Orthorhombic symmetry

4.5.1 Energy

To explore the spectroscopic properties of low-symmetry centres the case of an orthorhombic crystal field in addition to a tetragonal field was considered. In this restriction to \( \beta = \pm 90^\circ \) a cubic field was left outside consideration. The second-order operator corresponding to the orthorhombic field is written as

\[
H_{\text{or}} = \frac{1}{6} \sqrt{3} \left( J_z^2 + J_y^2 \right)
\]  

(4.12)

and is normalised with respect to the tetragonal operator \( H_{\text{te}} \). The general expression for the mixed tetragonal/orthorhombic field is

\[
H_{\text{cf}} = V_{\text{cf}} H_{\text{teor}},
\]

(4.13a)

with

\[
H_{\text{teor}} = \cos \gamma H_{\text{te}} + \sin \gamma H_{\text{or}}.
\]

(4.13b)

Variation of parameter \( \gamma \) over the range \( 0^\circ < \gamma < +30^\circ \) is sufficient to cover all basically different fields. Energies of the eight doublet states obtained from the diagonalisation of Hamiltonian (4.13) are given in figure 4.8 as a function of parameter \( \gamma \). It is noted that level crossings do not appear. For positive \( V_{\text{cf}} \), the expected case, the level related to the state \( |J = 15/2, m_J = \pm 1/2\rangle \) with the energy \( E = -21 \) at \( \gamma = 0^\circ \) will always be the ground state. In case of small non-axial distortion a perturbation treatment can be applied. It leads to the analytical expression

\[
E = V_{\text{cf}} \cos \gamma \left( -21 - \frac{441}{2} \tan^2 \gamma \right)
\]

(4.14)

for the energy of the lowest state. This is in good agreement with the numerically calculated curve but only up to some 3\(^\circ\). The wave function of the perturbed \( |\pm 1/2\rangle \) state is found to be

\[
|\pm 1/2\rangle' = |\pm 1/2\rangle - (1/2) \sqrt{35} \tan \gamma |\pm 5/2\rangle - 2 \sqrt{21} \tan \gamma |\pm 3/2\rangle
\]

(4.15)

in a non-normalised form. Similar expressions exist for other \( m_J \) values.
Figure 4.8 Energies of eight doublets in tetragonal axial field together with an orthorhombic crystal field calculated from equations (4.13a, b) with $V_c = +1$. Parameter $\gamma$, in the range $0^\circ \leq \gamma \leq +30^\circ$, controls the relative contributions of the two crystal fields.

### 4.5.2 $g$ Value

As before, the Zeeman effect is treated by diagonalization of the matrix $\langle m'_j | H_{ct} + H_{mf} | m''_j \rangle$. Principal values of the $g$ tensor in the Cartesian $x$, $y$, $z$ directions are drawn in figure 4.9 for the level derived from $m_j = \pm 1/2$ in tetragonal axial symmetry. Experimental data points for the OEr-1 centre observed in silicon are included in the figure [4.1]. A good agreement can be noted for $\gamma \approx 1.2^\circ$, providing confirmation for the assumed relation of the spectrum with the $J = 15/2$ of erbium.

With the wave function (4.15) for the ground state available, the Zeeman splitting can be calculated by treating it as a small perturbation. On this basis the expressions for the principal $g$ tensor components are

\begin{align}
g_x &= g_1 (+6\sqrt{7}c_{12}c_{12} + 4\sqrt{15}c_{32}c_{52} + 8c_{12}^2), \quad (4.16a) \\
g_y &= g_1 (-6\sqrt{7}c_{12}c_{12} + 4\sqrt{15}c_{32}c_{52} + 8c_{12}^2) \quad (4.16b)
\end{align}
\[ g_z = g_j (3c_{3/2}^2 - c_{5/2}^2 - 5c_{7/2}^2). \] 

(4.16c)

Inserting the wavefunction coefficients as following from equation (4.15) after their normalisation, and using \( g_j = 6/5 \), one obtains

\[ g_z = \frac{6}{5} \frac{8 - 84\sqrt{3}\ t\ t\gamma + 420\ t^2\ \gamma}{1 + \frac{371}{4} t^2\ \gamma}, \] 

(4.17a)

\[ g_x = \frac{6}{5} \frac{8 + 84\sqrt{3}\ t\ t\gamma + 420\ t^2\ \gamma}{1 + \frac{371}{4} t^2\ \gamma}, \] 

(4.17b)

and

\[ g_y = \frac{6}{5} \frac{1 - 833/4 t^2\ \gamma}{1 + \frac{371}{4} t^2\ \gamma}. \] 

(4.17c)

It is seen from figure 4.9 that the most sensitive indication for the non-axial distortion is given by the lifting of the \( g_z \) degeneracy, i.e., by \( g_x - g_z \). By equations (4.17) this difference equals

\[ g_x - g_z = \frac{1008/5 \sqrt{3} \ t\ t\gamma}{1 + \frac{371}{4} t^2\ \gamma}. \] 

(4.18)

With the experimental result for the Si-OEr-1 centre \( g_x - g_z = 7.15 \) its \( \gamma \) parameter is determined as \( \gamma = 1.2^\circ \).

4.6 Conclusions

Calculations have been performed of the electronic structure of the triply charged erbium ion in its spin–orbit ground level with spin \( J = 15/2 \) when embedded as an impurity in a host crystal. Calculations were carried out fully numerically. Employing a crystal field method the energy levels and wave functions were determined for the ion in Stark fields of cubic, trigonal, tetragonal and orthorhombic symmetry, created by the ligand ions of the crystal. The relative contributions of the crystal fields of isotropic, axial and non-axial
symmetry are described by mixing parameters $\alpha$, $\beta$, and $\gamma$. Also the principal components of $g$ tensors for the Zeeman splitting were calculated by applying a magnetic field in the appropriate directions.

In previous theoretical determinations of $g$ values, using analytical methods, exact results were restricted to the $\Gamma_6$ and $\Gamma_7$ states in pure cubic symmetry and the states $|J=15/2,m_s>$ in fields of pure axial character.

In contrast, in the numerical calculations fields of arbitrary structure can be constructed as the parameters $\alpha$, $\beta$, and $\gamma$ can be varied continuously over a range covering all situations.

Considering calculated results it is noted that the parallel principal $g$ value $g_\parallel$ in axial symmetry can change its sign upon variation of parameter $\beta$, governing the relative contributions of cubic and axial fields. Accepting a positive value for $g_\parallel$ in the purely axial situation of $\beta = +90^\circ$, where the quantisation of spin states is more straightforward, a negative value for $g$ appears in the cubic situation. In particular, for the $\Gamma_6$ state of cubic symmetry the consistent $g$ value is found as $g = -6$. In experiments the absolute value $g = 6$ will be measured.

From collected experimental data, obtained for a large number of varied host crystals, the trace $|g_\parallel + 2|g_z|$ of $g$ tensors for the erbium-related resonances was found often to be close to
20.4, i.e., the trace of the cubic centre in the $\Gamma_7$ state. An empirical rule of constant trace upon axial distortion with consequences for the electronic origin of the impurity states can be based on this observation. Such a rule has to be applied with care, however, as the real trace taking signs into account can be different from the measured trace based on absolute positive values. For instance, in case of axial symmetry, a real trace of $g_\parallel + 2g_\perp = -18$, based on $g_\parallel = +1.2$ and $g_\perp = -9.6$ and derived from $\Gamma_6$, is measured as a trace of 20.4 and interpreted as having a $\Gamma_7$ origin. In rare cases only, negative $g$ values have been concluded to for consistent analysis of experimental data, such as for the Yb ion in KMgF$_3$ [4.45].

Because of a complex dependence of $g$ values on crystal field parameters $\alpha$ and $\beta$, with often wide and sudden variations, the comprehensive summary of results is hard to give. Nevertheless, it is noted that over a wide range of $\alpha$ values, controlling the mixing of forth- and sixth-order cubic crystal fields, the trace of tensors remains remarkably constant upon a distortion with positive $\beta$ towards the $|J = 15/2, m_J = \pm 1/2>$ doublet. This accounts in an uncomplicated manner for the frequently observed tensors with trace near 20.4. One may conclude that the crystal-field approach provides a valid description of the spin system. It is also to be noted that equal or very similar $g$ values are calculated over a range of parameters. For the cubic centres, the $g$ values $g = 6$ for $\Gamma_6$ and $g = 6.8$ for $\Gamma_7$ do not depend at all on parameter $\alpha$. For the axial case, different combinations of parameters $\alpha$ and $\beta$ can give results not distinguishable by the experiments. Parameters $\alpha$ and $\beta$ are therefore not obtained from the analysis with great precision. Additional information is required for full characterization.

Such data could be provided by studies of the first excited state of the Stark splitting, such as the direct spectroscopic measurement of their Zeeman splitting, as reported, e.g., for the axial erbium center in CaF$_2$ [4.6]. In addition, from the population of this level as a function of temperature the excitation energy can be derived via the associated Boltzmann factor [4.6]. Alternatively, the position of the first excited states has been determined from the ground state resonance through the Orbach process of spin–lattice relaxation [4.15, 4.20 and 4.38]. More direct and more complete data on the position of the five to eight crystal-field split levels can come from the optical spectroscopy in the form of structure in the photoluminescence spectra, but this requires confirmation that the centers studied in both techniques are equal [4.46].

For interpretation of results from ODMR (optically detected magnetic resonance) calculations of the same nature as presented in this paper have to be extended to include the $J = 13/2$ first optically excited state at around 800 meV. Other topics for future research include the thorough investigation of centers of quartet $\Gamma_8$ character in cubic symmetry and the systematic exploration of $g$ tensors for low-symmetry centres in their $\alpha, \beta$ and $\gamma$ field of parameters.

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References


