Calculation of the orthorhombic $E$-parameter in EPR for $d^3$ spin systems

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Abstract

Third order perturbation theory is used to calculate the orthorhombic spin-Hamiltonian zero-field $E$-term for octahedrally surrounded $d^3$ spin systems ($S = 3/2$) in strong axial fields in the presence of a weak orthorhombic component.

Introduction

In this paper we present results of analytical third-order perturbation calculations of the zero-field splitting term $E$ for octahedrally surrounded $d^3$ ($S = 3/2$) systems, in the presence of strong and moderate axial fields and a weak orthorhombic perturbation, i.e. for $|D| \geq \hbar \nu$ and $|E| \leq \hbar \nu$, with $\nu$ the frequency of typically an EPR experiment. Expressions for $d^5$ ($S = 5/2$) systems were already derived before i.e., for the Fe$^{3+}$-V$_O$ system in SrTiO$_3$ [1, 2].

The ground state of $d^3$ ($S = 3/2$) ions in an octahedral field is $^4A_2$ [3-6]. All excited states are lying higher in energy by amounts large compared with the spin-orbit coupling. The $^4A_2$ state is connected through spin-orbit coupling with the excited $T_{2g}$ states only [2-7]. Use of second-order perturbation theory gives a $g$-value slightly less than 2. For axially distorted (tetragonal or trigonal) octahedrally surrounded $d^3$ spin systems the following spin-Hamiltonian is used [1-7]:

$$\mathcal{H} = S \cdot \vec{D} \cdot S + \mu_B H \cdot \vec{g} \cdot S$$  \hspace{1cm} (1)

The first term represents the zero-field splitting and the second term the Zeeman interaction. The spin degeneracy of the $^4A_2$ state is partly removed into two Kramers' doublets separated by $|2D|$. The principal contribution to the $g$-shifts is caused by mixing with the excited $^4T_{2g}$ state, which is split into an orbital singlet and an orbital doublet state. Mixing with the $^4T_{2g}$ state, interaction with other levels and spin-spin coupling leads to the observed zero-field splitting. If the zero-field splitting $|2D|$ is much larger than the Zeeman term, only one EPR transition within the Kramers doublet with $M_S = |\pm 1/2\rangle$ levels is observed. The angular dependence of the effective $g$-values can be obtained by perturbation theory within the $^4A_2$ term using as basis the $M_s = |\pm 3/2\rangle$ and $M_s = |\pm 1/2\rangle$ wave functions and is given by:

$$\mathcal{H} = D [S_z^2 - \frac{1}{3} S(S + 1)] + g_\parallel \mu_B HS_x \cos \alpha + g_\perp \mu_B HS_x \sin \alpha,$$  \hspace{1cm} (2)
with $\alpha$ the angle between the magnetic field $H$ and the centre axis $z$.

This is justified because the excited $T_2$ states are lying much higher in energy. The effective $g$-values in first order are given by $g^e_\parallel = g_\parallel$ and $g^e_\perp = 2g_\perp$ with an effective spin of $S' = \frac{1}{2}$ [1-7]. The angular dependence of the effective $g$-values are altered in second- and third-order perturbation theory by [1-2, 8-9]:

$$g^{\text{eff}}(\alpha) = (g^2_\parallel \cos^2 \alpha + 4g^2_\perp \sin^2 \alpha)^{\frac{1}{2}} \left[ 1 - \frac{3}{4} \left( \frac{g_\perp \mu_B H}{2D} \right)^2 F(\alpha) \right],$$

(3)

where $F(\alpha) = \sin^2 \alpha \left[ \frac{(4g^2_\parallel + 2g^2_\perp)\sin^2 \alpha - 2g^2_\parallel}{(4g^2_\perp - g^2_\parallel)\sin^2 \alpha + g^2_\parallel} \right]$. (4)

$\alpha$ is the angle between the magnetic field $H$ and the axial centre axis $z$ of the $d^3$ system and $\mu_B$ is the Bohr magneton.

Hence $g^{\text{eff}}(0^\circ) = g_\parallel$

**Spin Hamiltonian for an orthorhombic $S = 3/2$ system**

The spin-Hamiltonian for octahedrally surrounded orthorhombic distorted $d^3$ systems ($S = 3/2$) need an extension with the following term [1, 2]:

$$E(S_x^2 - S_y^2).$$

(5)

Using $\theta$ and $\delta$ as the polar angles of the magnetic field $H$ with respect to the main axis $z$ of the local centre we then obtain the following spin-Hamiltonian expressed in spin operators $S_z$ and $S_\pm = S_x \pm iS_y$,

$$\mathcal{H} = D \left( S_x^2 - \frac{1}{4} \right) + \frac{1}{2} E (S_x^2 + S_y^2)$$

$$+ \mu_B H \left[ g_\parallel S_x \cos \theta + \frac{1}{2} g_\perp (S_+ + S_-) \sin \theta \cos \delta - \frac{1}{2} i g_\parallel (S_+ + S_-) \sin \theta \sin \delta \right],$$

(6)

where it is understood that the level of zero energy is chosen so that the first term of eq. (6) is zero for the $S_z = \pm 1/2$ doublet. For systems with $|D| \gg h\nu$ the first term is taken as zero order Hamiltonian $\mathcal{H}_0$ and the other crystal field terms and the Zeeman splitting are treated as a perturbation $\mathcal{H}_1$. For values $h\nu/2|D| \geq 0.25$ one has to proceed with exact numerical computer calculations [3]. Using as basis the $|\pm 3/2\rangle$ and $|\pm 1/2\rangle$ wave functions, the matrix of the Hamiltonian is given by:
\[ H \]

| \(|+3/2\rangle\) | \(|+1/2\rangle\) | \(|−1/2\rangle\) | \(|−3/2\rangle\) |
|----------------|----------------|----------------|----------------|
| \(2D+3A\)      | \(\sqrt{3}\cdot B^*\) | \(\sqrt{3}\cdot E\) | 0              |
| \(\sqrt{3}\cdot B\) | \(A\)            | \(2B^*\)         | \(\sqrt{3}\cdot E\) |
| \(\sqrt{3}\cdot E\) | \(2B\)           | -\(A\)           | \(\sqrt{3}\cdot B^*\) |
| 0              | \(\sqrt{3}\cdot E\) | \(\sqrt{3}\cdot B\) | 2D-3A          |

with: \(A = \frac{1}{2}g_{\mu B}H\cos\theta\)
\(B = \frac{1}{2}\mu_BH\sin\theta(g_x\cos\delta+i g_y\sin\delta)\)
\(B^* = \frac{1}{2}\mu_BH\sin\theta(g_x\cos\delta-i g_y\sin\delta)\) and
\(\mu_B\) the Bohr magneton.

The eigenvalues of \(H_0\) are doubly degenerate and \(H_1\) couples via \(B\) and \(B^*\) between eigenstates within the same eigenspace with energy zero. The basis of this eigenspace has first to be adapted such that the submatrix of \(H\) within the eigenspace \(|±1/2\rangle\) becomes diagonal.

The new wave functions then become:

\[
|\gamma\rangle = c_1|+\frac{1}{2}\rangle + c_2|−\frac{1}{2}\rangle \quad \text{and} \quad |\delta\rangle = -c_2|+\frac{1}{2}\rangle + c_1^*|−\frac{1}{2}\rangle,
\]
where

\[
c_1 = \left[\frac{B^*}{B}\right]^{1/2} \cdot \left[\frac{(A^2+|2B|^2)^{1/2}+A}{2(A^2+|2B|^2)^{1/2}}\right] = \left[\frac{P+A}{2P}\right] \cdot \left[\frac{B^*}{B}\right]^{1/2}
\]
and

\[
c_2 = \left[\frac{P-A}{2P}\right]^{1/2}
\]

The energies are:

\[
W_{\gamma,\delta} = \pm(A^2+|2B|^2)^{1/2} = \pm P.
\]

The above matrix transforms within the new basis as,

| \(|+3/2\rangle\) | \(|\gamma\rangle\) | \(|\delta\rangle\) | \(|−3/2\rangle\) |
|----------------|----------------|----------------|----------------|
| \(2D+3A\)      | \(c_1\sqrt{3}\cdot B^*+c_2\sqrt{3}\cdot E\) | \(c_1^*\sqrt{3}\cdot E-c_2\sqrt{3}\cdot B^*\) | 0              |
| \(|\gamma\rangle\) | \(+P\)            | 0              | \(c_1^*\sqrt{3}\cdot E+c_2\sqrt{3}\cdot B^*\) |
| \(|\delta\rangle\) | \(c_1\sqrt{3}\cdot E-c_2\sqrt{3}\cdot B\) | 0              | \(-P\)          |
| \(|−3/2\rangle\) | \(c_1\sqrt{3}\cdot E+c_2\sqrt{3}\cdot B\) | \(c_1^*\sqrt{3}\cdot B-c_2\sqrt{3}\cdot E\) | 2D-3A          |

If \(E = 0\), second-order perturbation does not split the \(|\gamma\rangle\) and \(|\delta\rangle\) levels further. With \(E \neq 0\), an
additional splitting is caused by the admixture of $|\pm 3/2\rangle$ levels into the ground states $|\gamma\rangle$ and $|\delta\rangle$ and is given by:

$$
\Delta W_{\gamma}^{(2)} = -\sum_{\gamma \neq 3/2} \frac{(3/2|\gamma\rangle\langle\gamma| \gamma + 3/2)}{(W_{\gamma} + 3/2 - W_{\gamma})} = -\sum_{\gamma \neq -3/2} \frac{(3/2|\gamma\rangle\langle\gamma| \gamma - 3/2)}{(W_{\gamma} - 3/2 - W_{\gamma})} \tag{10}
$$

This gives:

$$
\Delta W_{\gamma}^{(2)} = \frac{-6\mu_{B}E(c_{1}B + c_{1}B^*)}{2D} = -\Delta W_{\delta}^{(2)}
$$

$$
\Delta W_{\gamma}^{(2)} - \Delta W_{\delta}^{(2)} = -\frac{6\mu_{B}E(c_{1}B + c_{1}B^*)}{D} = -\frac{6E}{D} \sin^{2}\theta \frac{(g_{2}^{2}\cos^{2}\delta - g_{2}^{2}\sin^{2}\delta)}{(g_{2}^{2}\cos^{2}\delta + 4g_{1}^{2}\sin^{2}\delta)^{1/2}} \tag{11}
$$

In third-order perturbation theory $\Delta W_{\gamma}^{(3)}$ is given by [10],

$$
\Delta W_{\gamma}^{(3)} = \sum_{m \neq \gamma, \delta} \frac{\mathcal{H}_{mm}}{(W_{m} - W_{\gamma})} \left( \mathcal{H}_{mm} - \mathcal{H}_{\gamma \gamma} \right) + \sum_{m \neq \gamma, \delta} \sum_{p \neq m, \gamma, \delta} \frac{\mathcal{H}_{mp} \mathcal{H}_{\gamma p}}{(W_{p} - W_{\gamma})(W_{m} - W_{p})} \tag{12}
$$

where $m$ is the ground state.

The second term is equal to zero, because according to $\sum_{m \neq \gamma, \delta}$ the wave functions $\gamma$ and $\delta$ may not be used as variables and matrix elements $\mathcal{H}_{mp} \cdot \mathcal{H}_{\gamma p}$ give zero.

The first term gives the following result,

$$
\Delta W_{\gamma}^{(3)} = \frac{3BB^*}{2D} - \frac{3PBB^*}{4D^2} + \frac{9A^2BB^*}{4D^2P} \tag{13}
$$

For systems with $E < D$, the terms in $E/D$, $E/D^2$, $E^2/D$ and $E^3/D$ are small and are therefore omitted, therefore $\Delta W_{\gamma}^{(3)} = -\Delta W_{\gamma}^{(2)}$.

We are now able to give the expression for the g-value, which is as follows,

$$
g^{eff} \mu_{B}H = W_{\gamma} + \Delta W_{\gamma}^{(2)} + \Delta W_{\gamma}^{(3)} - W_{\delta} - \Delta W_{\delta}^{(2)} - \Delta W_{\delta}^{(3)} = 2P + 2\Delta W_{\gamma}^{(2)} + 2\Delta W_{\gamma}^{(3)} \tag{15}
$$

After some calculations we obtain:

$$
g^{eff}(\theta) = (g_{2}^{2}\cos^{2}\theta + 4g_{1}^{2}\sin^{2}\theta)^{1/2} \left[ 1 - \frac{3}{4} \left( \frac{g_{2}^{2}\mu_{B}H}{2D} \right) \right] F(\theta) - \frac{6E}{D} \sin^{2}\theta \frac{g_{2}^{2}\cos^{2}\delta - g_{2}^{2}\sin^{2}\delta}{(g_{2}^{2}\cos^{2}\theta - 4g_{1}^{2}\sin^{2}\theta)^{1/2}} \tag{16}
$$

where

$$
F(\theta) = \sin^{2}\theta \left( \frac{(4g_{2}^{2} + 2g_{2}^{2})\sin^{2}\theta - 2g_{2}^{2}}{(4g_{1}^{2} - g_{2}^{2})\sin^{2}\theta + g_{2}^{2}} \right) \quad \text{and} \quad g_{2}^{2} = g_{2}^{2}\cos^{2}\delta + g_{2}^{2}\sin^{2}\delta
$$

The expression for the axial field (with $E = 0$) is given by eq. (3).
The results obtained above were used in a study of the non-cubic Fe$^{5+}$ centre in SrTiO$_3$ [2, 11]. In the extreme case, where the Zeeman term dominates the axial field, see eq. (1), the solutions are given by references [4, 7]. Examples of the latter are the SrTiO$_3$:Mo$^{3+}$ [12] and SrTiO$_3$:Cr$^{3+}$ systems [2, 13].

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