

State Mixing and the Cubic Crystal Field Approximation for Rare Earth Ions: The Case of Er³⁺ in Tetrahedral Semiconductors

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Abstract

The validity of the cubic crystal field (CCF) approximation for the interpretation of the Er³⁺ ion in sites with tetragonal and trigonal symmetry is examined. The ground state paramagnetic resonance principal g values are explicitly calculated in terms of the cubic crystal field eigenstates as a function of axial crystal field strength. It is shown that depending on the ground state crystal field eigenstate, the widely accepted CCF approximation of taking the average of the trace of the g tensor and equating it to the g value found in cubic symmetry can lead to a misinterpretation of the ground Stark level and the lattice site of the ion. The implication for experimentally reported results is discussed.

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I Introduction

The lattice location and coordination of rare earth (RE) ions in semiconductors and insulators has been to the forefront of spectroscopy research for many years. [1, 2] The different electronic configurations of the ions, coupled with the inner $4f$ shell electrons being largely shielded from the host crystal field, results in sharp luminescence transitions. The narrowness of the optical emission coupled with an insensitivity of the emission wavelength to the host material has resulted in rare earth ions being used in lasers, fibre amplifiers and in optical communications. Optimising the concentration of optically active ions is crucial for the use of RE ions as luminescence centres and knowledge of the electronic properties of the ions can aid in the improvement of devices. [2, 3] The shielding of the RE ion from the host semiconductor is also attractive for potential applications in quantum computing with the possibility of exploiting long coherence times associated with the weak spin – lattice interactions [4]. To that end it is often necessary to employ a range of techniques that are capable of identifying the ion, the lattice location and/or coordination. Measurements of the g value in electron paramagnetic resonance (EPR) [5, 6] as well as Zeeman measurements [7] are able to distinguish between different RE ions. In a site with cubic symmetry a spin $\frac{1}{2}$ centre will produce a single isotropic g value, g_c . For RE centres with less than cubic symmetry the cubic crystal field (CCF) approximation [8] is widely employed in which average of the trace of the g tensor, g_{av} , i.e. $g_{av} = 1/3(g_{xx} + g_{yy} + g_{zz})$ is compared with g_c . When g_{av} is close to g_c , this is often taken as proof of the identity of the ion and the lattice site. Despite being extensively employed [5, 8, 9] a number of apparently anomalous results have been published which have led to a questioning of the use of the CCF approximation. The main aim of this paper is to examine the validity of the CCF approximation for the trivalent erbium ion in sites with tetragonal and trigonal symmetry and compare with published experimental results. Amongst all the RE ions, Er^{3+} , has received particular attention as there is an optical transition occurring at around the technologically important wavelength of $1.5 \mu\text{m}$.

II Trivalent Erbium in a Cubic Crystal Field

The Er^{3+} ion consists of eleven $4f$ electrons which results in a total spin quantum S of $3/2$, orbital quantum number L of 6 and total angular momentum quantum number, J , of $15/2$. The 16-fold degenerate ${}^4I_{15/2}$ spin-orbit (SO) ground state level is separated by about 6500 cm^{-1} from the ${}^4I_{13/2}$ first excited SO state. The incorporation of an Er^{3+} ion in a host semiconductor with T_d symmetry results in the formation five Stark levels consisting of two Kramers doublets (Γ_6 and Γ_7) and three quartets (Γ_8), where each Γ represents the respective irreducible representations of the double cubic group. Note that the Γ_6 and Γ_7 levels only occur once. The ordering of the Stark levels is determined by the relative strength of the fourth and sixth order crystal field terms in the cubic crystal field Hamiltonian [8]

$$H_{cubic} = B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4), \quad (1)$$

where O_n^m are the symmetry related crystal field equivalent operators associated with each quantum number J . The coefficients B_4 and B_6 determine the magnitude of the crystal field splitting, as a result of the arrangement of the surrounding cations and anions, and are related to the fourth and sixth order potentials via

$$B_4 = \beta A_4 \langle r^4 \rangle \text{ and } B_6 = \gamma A_6 \langle r^6 \rangle, \quad (2)$$

where $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$ can be calculated by a point charge calculation [8] or by the superposition method [10] and the values of β and γ depend upon L , S and J and have been tabulated elsewhere [11]. In the seminal work by Lea, Leask and Wolf [12] it was shown that solution to the Hamiltonian in Eq. (1) can be obtained using the substitutions

$$B_4 F_4 = Wx \text{ and } B_6 F_6 = W(1 - |x|), \quad (3)$$

where F_4 and F_6 are numerical factors chosen to keep the fourth and sixth order matrix elements in the same numerical range; for Er^{3+} , $F_4 = 60$ and $F_6 = 13,860$. The parameter x is the crystal field mixing term related to the ratio of B_4 to B_6 and runs from -1 to $+1$ and the spacing between the

energy levels is controlled by W . For $W > 0$, the Γ_7 level will lie lowest between $-1 < x < -0.46$, the Γ_6 level will lie lowest between $-0.46 < x < 0.58$ and for $x > 0.58$ the lowest energy state will be Γ_8 . As an example an Er^{3+} ion located at a Zn^{2+} substitutional site in zineblende ZnSe produces a value of $A_4 \langle r^4 \rangle = -44.7 \text{ cm}^{-1}$ and $A_6 \langle r^6 \rangle = 2.1 \text{ cm}^{-1}$ using a point charge model which in turn would give a value of $x = -0.67$ and $W = 0.18 \text{ cm}^{-1}$. The sign of x can distinguish between a substitutional site and an interstitial site reflecting the different arrangement of the cations and anions. [13] Note the value of x reflects the ratio of B_4/B_6 and as such the choice of formal charges of the cations and anions does not strongly affect the value of x though it will have an affect on W .

Application of a magnetic field results in the lifting of the Kramers degeneracy however as the strength of the Zeeman interaction is small when compared with the magnitude of the crystal field, a perturbative approach in calculating the g values from the crystal field eigenstates is employed. In general, the crystal field eigenstates $|\psi\rangle$, and the time reversed state $|\psi'\rangle$, are a normalized superposition of the $|m\rangle$ states associated with the quantum number J with the values of m running from $-J$ to $+J$ and are given by

$$|\psi\rangle = \sum_m c_m |m\rangle \text{ and } |\psi'\rangle = \sum_m (-1)^{J-m} c_m^* | -m\rangle \quad (4)$$

where $\sum_m |c_m|^2 = 1$. The presence of O_n^4 operator terms in Eq. (1) ensures that the highest m -fold rotation axis present is a four-fold axis and as a result the various terms of $|m\rangle$ that appear in the wavefunction expansion will each differ by four. Diagonalisation of the Hamiltonian in Eq. (1) using Eq. (3) gives the crystal field eigenstates for Γ_6 and Γ_7 levels as

$$\Gamma_6: 0.6332 \left| \pm 13/2 \right\rangle + 0.5819 \left| \pm 5/2 \right\rangle - 0.4507 \left| \mp 3/2 \right\rangle - 0.2393 \left| \mp 11/2 \right\rangle \text{ and} \quad (5a)$$

$$\Gamma_7: 0.5818 \left| \pm 15/2 \right\rangle + 0.3307 \left| \pm 7/2 \right\rangle + 0.7182 \left| \mp 1/2 \right\rangle + 0.1910 \left| \mp 9/2 \right\rangle. \quad (5b)$$

The g value in cubic symmetry, g_c , can be calculated from the matrix element $2g_J \langle \psi | J_z | \psi \rangle$, using the wavefunctions in Eq. (5) above, where a value of the Landé g value, g_J , of $6/5$ is used.

For the Γ_6 and Γ_7 Stark levels the g values in cubic symmetry are 6.8 and 6.0, respectively. It is important to note here that coefficients of the $|m\rangle$ states in Eq. (5) do not depend on the strength of the crystal field. This is a result of the Γ_6 and Γ_7 irreducible representations only appearing once in the decomposition of the $J=15/2$ spin-orbit state. [8] For example for $-1 < x < -0.46$ the ground state will be Γ_7 and is independent of x so the g value will be 6.0 for all values of x in this range. A similar argument can be applied to the Γ_6 stated when $-0.46 < x < 0.58$. This point is highlighted here as the analysis of the g values in the presence of an axial crystal field will not also require the cubic crystal field terms to be changed.

If the symmetry of the rare earth ion site is axial then instead of a single g value, a g tensor with principal g values g_{\parallel} and g_{\perp} is used, where g_{\parallel} is taken along the axial z direction and g_{\perp} refers to the plane perpendicular to z . If the total crystal field can be considered as predominantly cubic with an additional axial component superimposed, then within the CCF approximation the average of the trace of the g tensor, g_{av} , defined as $g_{av} = 1/3(g_{\parallel} + 2g_{\perp})$ will equal the g value in cubic symmetry g_c i.e. 6.8 for Γ_6 and 6.0 for Γ_7 , respectively. The solid lines in **Figure 1** show how the principal g values must vary along with some reported values from the literature [5]. Figure 1 shows that from a range of samples the predicted g values appear to follow the pattern predicted by the line associated with the Γ_6 or Γ_7 state, respectively. However, there is a greater tendency for more data points to lie on the line associated with the Γ_6 state, corresponding to an average g value of 6.8. There are also a smaller number of data points at the lower values of g_{\perp} . In order to investigate this behaviour we have calculated the g values as a function of axial crystal field strength.

III Effect of the Axial Crystal Field

If the overall crystal field deviates strongly from cubic symmetry then more terms are added into the Hamiltonian. For example in a strongly tetragonal crystal field five terms involving $B_2^0, B_4^0, B_4^4, B_6^0, B_6^4$ are required. When the crystal field is cubic there are inter-relationships between

these terms with $B_4^0 = B_4, B_4^4 = 5B_4$ and $B_6^0 = B_6, B_6^4 = -21B_6$. These give the simplified form of Eq. (1). However in tetragonal crystals these relationships breakdown and it is necessary to calculate or fit from optical measurements each of the five B_n^m parameters independently. The subject of this paper is where an axial crystal field is superimposed upon crystal field with predominantly cubic symmetry – the cubic crystal field approximation. In the CCF approximation an axial crystal field term $B_2O_2^0$ is simply added to the cubic Hamiltonian to give

$$H_{tetra} = B_2O_2^0 + B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4), \quad (6)$$

with $B_2 = \alpha A_2 \langle r^2 \rangle$ as before [11]. Numerical diagonalisation of Eq. (6) gives for a Γ_7 crystal field eigenstate of the form

$$|\psi_1 \rangle = a_1 |15/2\rangle + b_1 |7/2\rangle + c_1 |-1/2\rangle + d_1 |-9/2\rangle \quad (7)$$

The principal g values are given by

$$g_{\parallel} = 2g_J (\langle \psi | J_z | \psi \rangle) \quad \text{and} \quad g_{\perp} = g_J (\langle \psi | J_+ + J_- | \psi \rangle). \quad (8)$$

where the coefficients $a_1 \dots d_1$ now depend on the value of the axial crystal field B_2 . Application of the ladder operators in Eq. 8 to the wavefunction in Eq. 7 gives the following expressions for the principal g values

$$g_{\parallel,1} = g_J (15a_1^2 + 7b_1^2 - c_1^2 - 9d_1^2) \quad \text{and} \quad (9a)$$

$$|g_{\perp,1}| = 2g_J (\sqrt{48} b_1 d_1 + 4c_1^2). \quad (9b)$$

The variation of the principal g values for a Γ_7 ground state over a wide range of axial crystal fields is shown in **Figure 2a**. The two curves cross at zero axial crystal field with a g value of 6.0 as calculated earlier. High values of g_{\parallel} (i.e. those larger than 8) can be obtained with even low values of negative axial crystal field whereas at more negative axial crystal fields, the value g_{\parallel} tends to saturate around 18. In the same range of axial crystal fields the value of g_{\perp} approaches zero; indeed the value of g_{\perp} is below 2 for axial crystal fields below -16 cm^{-1} . Since the intensity of the EPR

transition is governed by the strength of the matrix element associated with g_{\perp} , these transitions will not be observable. We believe this explains the low number of data points at high values of g_{\parallel} in Figure 1.

A second observation can be made from Figure 2a; for axial crystal fields larger than 30 cm^{-1} the value of g_{\parallel} is less than zero. The sign of the g value in EPR can be measured if circularly polarized microwave radiation is used to induce spin flip transitions. However, most experiments employ linearly polarized radiation which is not sensitive to the sign of the g value and this can lead to a misleading calculation of the average g value as demonstrated in **Figure 2b** where the average g value calculated using the both the real (i.e. negative) and absolute values of g_{\parallel} found in Figure 2a is shown. For axial crystal fields larger than 30 cm^{-1} , Figure 2(b) shows that the average g value appears to deviate from that predicted if the CCA approximation holds if the absolute value of g_{\parallel} is used. For an axial crystal field of 60 cm^{-1} , $g_{\text{av}} = 6.51$ and at larger axial crystal fields ($\sim 150 \text{ cm}^{-1}$), g_{av} reaches 6.70 before leveling off. *It is in this regime that it may appear that the average g value is now reminiscent of that associated with a Γ_6 state, rather than the actual Γ_7 state.* As a result care must be employed when interpreting the average g value in this case and the large number of data points with $g_{\text{av}} \sim 6.8$ in Figure 1 is proof of this.

It is our contention that an observed average g value of between 6.0 and 6.8 is due to the influence of the axial crystal field on the Γ_7 level. However, there are two well known interactions that can alter the g value: the orbital – lattice interaction due to covalency effects [14] or crystal field mixing of higher lying states [10]. The effects of covalency are described in terms of modifications of the Landé g value g_J , through the introduction of the orbital reduction factor [15], usually expressed as $(1-k)$ as

$$g'_J = g_J - (1-k) \frac{J(J+1) - S(S+1) + L(L+1)}{2J(J+1)}. \quad (10)$$

Using the value of the quantum numbers J , L and S discussed above, a reduction of the cubic g value from 6.8 level to, say, 6.2 would require a value of $(1 - k)$ of 0.1323. This value can be

compared with a value of $(1 - k)$ for other rare earth ions such as Yb^{3+} or Dy^{3+} in CaO where a value of 0.02 and 0.04, respectively, is required. [15] In the first row transition metal series, much larger orbital lattice reduction factors of 0.2 has been reported for Fe^{2+} and 0.3 for Ti^{3+} (see ref. 16). As such we do not believe that the large values of $(1 - k)$ required to change a cubic g value from 6.8 to 6.2 is likely to occur in the rare earth series and we discount this as a significant contribution. The second mechanism involves the admixture into the ground state Γ by the crystal field of other states with the same irreducible representation but in higher lying J manifolds. The crystal field could mix in the Γ_7 level originating from the ${}^4I_{13/2}$ excited with the Γ_7 level in the ${}^4I_{15/2}$ ground state. Kingsley and Aven [17] suggested that the g value associated with the Γ_7 level in the presence of this crystal field mixing takes the form

$$g(\Gamma_7) = 2(1 - \alpha^2)g_J \langle \Gamma_7({}^4I_{15/2}) | J_z | \Gamma_7({}^4I_{15/2}) \rangle + 2\alpha^2 g_J^* \langle \Gamma_7({}^4I_{13/2}) | J_z | \Gamma_7({}^4I_{13/2}) \rangle \quad (11)$$

where g_J and g_J^* are the Landé g value for the Γ_7 level in the ground ${}^4I_{15/2}$ spin-orbit level (with $g_J = 1.2$) and first excited ${}^4I_{13/2}$ SO state (with $g_J^* = 1.108$). In this case α represents the admixture between the two states. A value of $\alpha = 0.33$ would be required to lower a g value from 6.0 to say 5.95 which since the ${}^4I_{13/2}$ and ${}^4I_{15/2}$ states lie 6500 cm^{-1} apart would require a crystal field matrix element of over 2140 cm^{-1} - which is unreasonably large in the rare earth ion series. Similarly arguments would preclude the Γ_6 state being significantly reduced from 6.8. As such we believe that neither of these two mechanisms is responsible for significant changes in the average g value.

Having concluded that an upward shift in the g value from 6.0 toward 6.7 or 6.8 is not due to covalency or crystal field induced admixtures of states, we turn to other possible reasons by examining how each of the individual coefficients a_1 to d_1 in Eq. (7) varies with axial crystal field (**Figure 3**). It is apparent that the largest variations amongst the coefficients occurs with a_1 and c_1 with both b_1 and d_1 having a smaller much contribution. From Eq. (9a) we can see that the

variation of $g_{\parallel,1}$ with axial crystal field is based on the competing behaviour of $15a_1^2$ compared with $-c_1^2$. Clearly the larger prefactor associated with the $|\pm 15/2\rangle$ coefficient controls the overall behaviour and hence the similarity in the trend of $g_{\parallel,1}$ in Figure 2a and the coefficient a_1 in Figure 3. In the case of g_{\perp} , inspection of Eq. (9b) shows that $g_{\perp,1}$ does not depend on a_1 and its behaviour with crystal field is governed by c_1^2 with a small contribution from b_1d_1 . As c_1 goes to zero for axial crystal fields less than about -100 cm^{-1} the value of $g_{\perp,1}$ goes to zero as well and the overall crystal field eigenstates are now mainly controlled by the $|\mp 1/2\rangle$ component of the overall crystal field eigenstates. We believe that it is this mixing between the two dominant states $|\pm 15/2\rangle$ and $|\mp 1/2\rangle$ that controls the g value.

Being able to predict when this strong mixing occurs will be of importance in knowing when the interpretation from CCF approximation can be believed using linearly polarized radiation. The axial O_2^0 operator transforms as $3J_z^2 - J(J+1)$ within a constant J manifold. The four components in $|\psi_1\rangle$, associated with the Γ_7 state, have matrix element values of 105 for the $|\pm 15/2\rangle$ state, -27 for $|\pm 7/2\rangle$, -63 for $|\mp 1/2\rangle$ and -3 for $|\mp 9/2\rangle$ states which results in a clear imbalance between the weightings of the coefficients. For the case of the Γ_6 level the corresponding O_2^0 matrix elements are 21 for the $|\pm 13/2\rangle$ state, -15 for $|\pm 5/2\rangle$, -19 for $|\mp 3/2\rangle$ and -9 for $|\mp 11/2\rangle$. This is a more balanced wave function in terms of coefficients and the corresponding g values should satisfy the CCF approximation. In order to test this assumption we have calculated the principal g values associated with the Γ_6 level as a function of axial field. The wave function derived from a Γ_6 state in an axial field can be expressed as

$$|\psi_2\rangle = a_2|\pm 13/2\rangle + b_2|\pm 5/2\rangle + c_2|\mp 3/2\rangle + d_2|\mp 11/2\rangle. \quad (12)$$

The principal g values in this case are

$$g_{\parallel,2} = g_J(13a_2^2 + 5b_2^2 - 3c_2^2 - 11d_2^2) \text{ and} \quad (13a)$$

$$|g_{\perp,2}| = 2g_J(\sqrt{28}a_2d_2 + \sqrt{60}b_2c_2) \quad (13b)$$

The variation of these g values (**Figure 4a**) and average g value (**Figure 4b**) with axial crystal field shows that the two principal g values do not deviate significantly from that predicted for a Γ_6 state in cubic symmetry (6.8) as shown in Figure 4. Furthermore over the course of $\pm 200 \text{ cm}^{-1}$ variation in the axial field, the average g value remains within 0.1 of the predicted 6.8 for a Γ_6 ground state in accordance with our assumption in relation to the CCF approximation. Finally, we note how the magnitude of the difference in the g values, $|g_{\parallel} - g_{\perp}|$, for the Γ_6 state scales linearly with axial field up to 200 cm^{-1} with a slope of $0.02/\text{cm}^{-1}$ (**Figure 5**). However, we do not find such a linear relationship with axial crystal field for the Γ_7 state. As such the approximation that the magnitude of the difference in g values is not a good measure of the strength of the axial crystal field when strong state mixing occurs.

Finally, it is possible to extend this approach for Er^{3+} in sites with trigonal symmetry. The Hamiltonian for a rare earth ion in trigonal symmetry takes the form

$$H_{\text{trig}} = B_2O_2^0 + B_4\left(-\frac{2}{3}O_4^0 + \frac{40\sqrt{2}}{3}O_4^3\right) + B_6\left(\frac{16}{9}O_6^0 + \frac{140\sqrt{2}}{9}O_6^3 + \frac{154}{9}O_6^6\right) \quad (14)$$

The presence of O_n^3 terms ensures that the highest n-fold axis present is now a three fold axis and the form of the Hamiltonian above is one in which the trigonal axis is pointing along an equivalent $\langle 111 \rangle$ direction. This will mean that the various value of $|m\rangle$ that appear in the wavefunction expansion will differ by 3. For the Γ_7 state in trigonal symmetry the wavefunction is

$$|\psi_3 \rangle = a_3|15/2\rangle + b_3|9/2\rangle + c_3|3/2\rangle + d_3|-3/2\rangle + e_3|-9/2\rangle + f_3|-15/2\rangle. \quad (15)$$

We calculate $g_{\parallel,3} = 3g_J(5a_3^2 + 3b_3^2 + c_3^2 - d_3^2 - 3e_3^2 - 5f_3^2)$, however as no $|m\rangle$ term in $|\psi_3\rangle$ differs by one from $|\psi_3'\rangle$ the value of $g_{\perp,3}$ will equal zero and no transition will be seen. The wavefunction for a Γ_6 state in trigonal symmetry will be

$$|\psi_4\rangle = a_4\left|13/2\right\rangle + b_4\left|7/2\right\rangle + c_4\left|1/2\right\rangle + d_4\left|-5/2\right\rangle + e_4\left|-11/2\right\rangle, \quad (16a)$$

and we calculate that the corresponding principal g values will be

$$g_{\parallel,4} = g_J(13a_4^2 + 7b_4^2 - c_4^2 - 5d_4^2 - 11e_4^2) \text{ and } |g_{\perp,4}| = 2g_J(-\sqrt{28}a_4e_4 + \sqrt{55}b_4d_4 - 4c_4^2). \quad (16b)$$

We find as in the case of Γ_6 in tetragonal symmetry, that the average g value does not differ significantly from 6.8.

Conclusions

We have investigated the validity of the cubic crystal field approximation for the trivalent rare earth ion erbium in the presence of an axial crystal field. We have calculated the principal g values associated with the crystal field ground state doublets (Γ_6 and Γ_7) as a function of axial crystal field strength and shown that the cubic crystal field approximation holds for the Γ_6 ground state regardless of the type of microwave radiation used. However, for the Γ_7 eigenstate circularly polarized radiation should be used. To know if the choice of radiation is important it is necessary to examine how the axial crystal field operator O_2^0 transforms for each of the components $|m\rangle$ in the wavefunction expansion. We believe that balanced wave functions obey the cubic crystal field approximation well and using circularly polarized microwave radiation is able to resolve this problem.

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- ¹³ In both T_i and T_s sites the nearest neighbour (nn) atoms lie $\sqrt{3}a/4$ from the ion in equivalent $\langle 111 \rangle$ directions, where a is the lattice constant of the host semiconductor. In the T_s site the 12 next nearest (nnn) atoms lie in $\langle 110 \rangle$ directions are at a distance of $a/\sqrt{2}$. This differs from the case of T_i site in which the 6 nnn atoms lying in the $\langle 100 \rangle$ directions are at a distance of $a/2$.

This is only 15% further out than the nn atoms and it is the octahedral field from these 6 nn atoms that stabilizes the ion position.

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Figure captions

Figure 1 Solid lines show the variation of g_{\perp} with g_{\parallel} for Er^{3+} assuming either Γ_6 or Γ_7 ground state. Symbols are experimentally measured values in a range of hosts taken from reference 5.

Figure 2 (a) Variation of principal g values g_{\parallel} and g_{\perp} as a function of axial crystal field for a state originating with a Γ_7 cubic ground state. (b) The average of the trace of g tensor, g_{av} , as calculated from (a) using the real value and absolute value of g_{\parallel} . The open circles refer to data when the absolute magnitude of g_{\parallel} is used and the solid line when the real g value is used.

Figure 3 Variation of the coefficients a_1 to d_1 for a Γ_7 ground state as a function of axial crystal field. Note the rapid variation of a_1 with crystal field and the similar rapid change of g_{\parallel} in Fig 2a.

Figure 4 (a) Variation of principal g values $g_{\parallel,2}$ and $g_{\perp,2}$ as a function of axial crystal field for a state originating with a Γ_6 cubic ground state. (b) The average of the trace of g tensor, g_{av} .

Figure 5 Variation of the difference in g values $|g_{\parallel} - g_{\perp}|$ for the both the Γ_7 and Γ_6 states. In the case of the Γ_6 state the difference in g values has a slope of $0.02/\text{cm}^{-1}$ which can then be used as a measure of the strength of the axial crystal field.

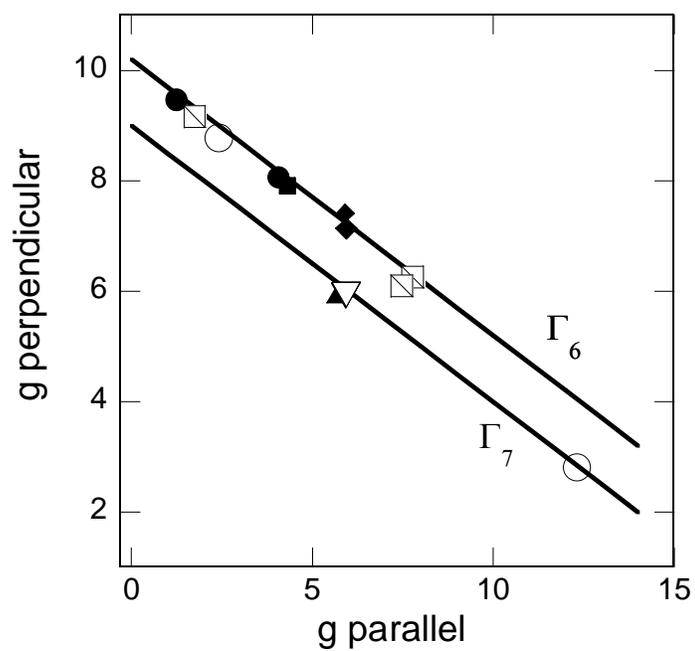


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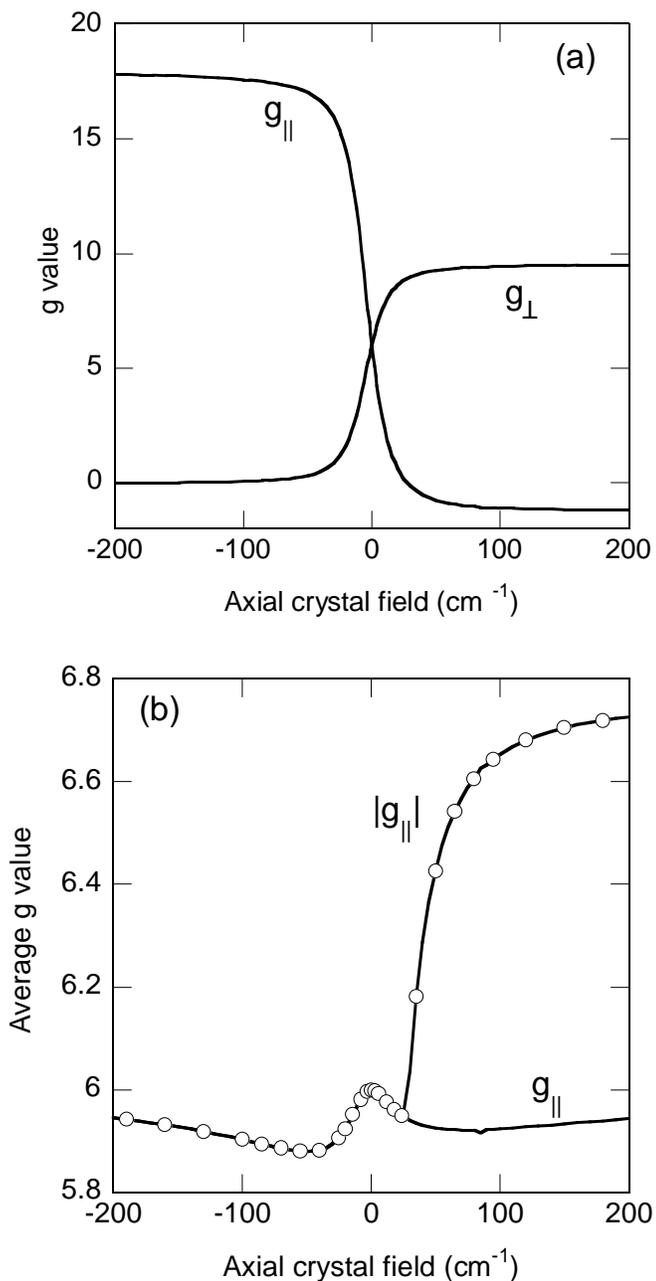


Figure 2 (a) Variation of principal g values g_{\parallel} and g_{\perp} as a function of axial crystal field for a state originating with a Γ_7 cubic ground state. (b) The average of the trace of g tensor, g_{av} , as calculated from (a) using the real value and absolute value of g_{\parallel} . The open circles to refer to data when the absolute magnitude of g_{\parallel} is used and the solid line when the real g value is used.

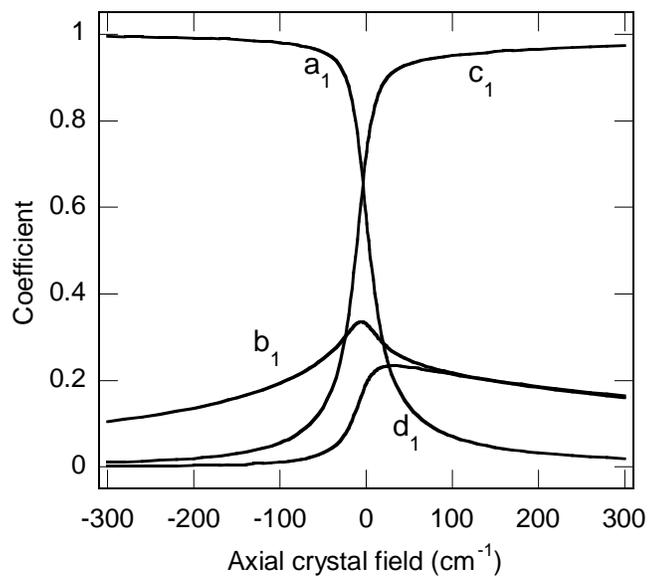


Figure 3 Variation of the coefficients a_1 to d_1 for a Γ_7 ground state as a function of axial crystal field. Note the rapid variation of a_1 with crystal field and the similar rapid change of g_{\parallel} in Fig 2a.

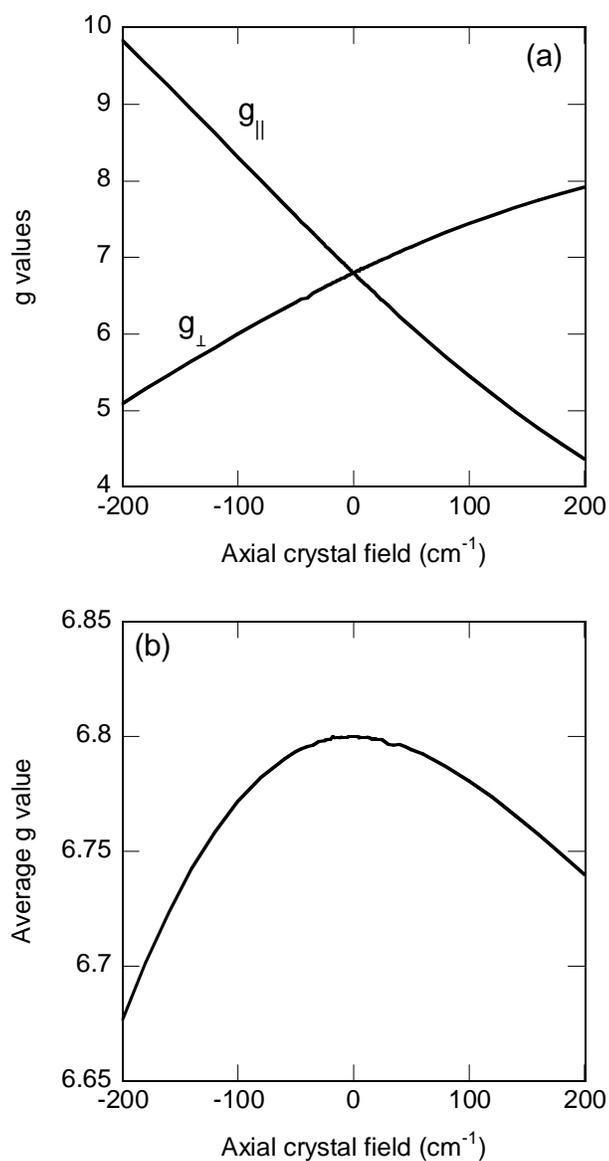


Figure 4 (a) Variation of principal g values $g_{\parallel,2}$ and $g_{\perp,2}$ as a function of axial crystal field for a state originating with a Γ_6 cubic ground state. (b) The average of the trace of g tensor, g_{av} .

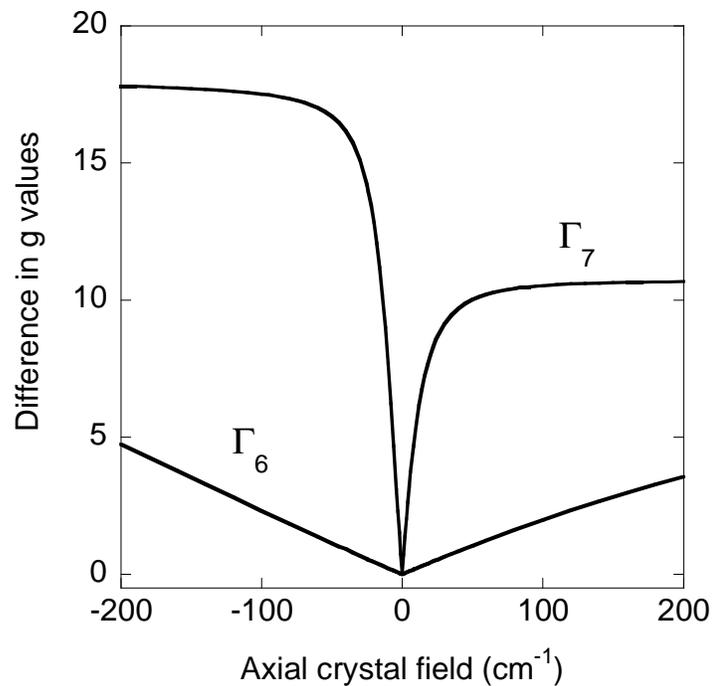


Figure 5 Variation of the difference in g values $|g_{\parallel} - g_{\perp}|$ for the both the Γ_7 and Γ_6 states. In the case of the Γ_6 state the difference in g values has a slope of $0.02/\text{cm}^{-1}$ which can then be used as a measure of the strength of the axial crystal field.