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State mixing and the cubic crystal field approximation for rare earth ions: the case of the Er^{3+} ion in axial crystal fields

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Abstract

The validity of the cubic crystal field (CCF) approximation for the interpretation of the magnetic resonance properties of the Er^{3+} ion in crystal fields 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 simply 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 state Stark level and the lattice coordination of the ion. The implications for experimentally reported results are discussed.

1. 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. Optimizing 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 when incorporated into suitable hosts can aid in the improvement of devices [2, 3]. The shielding of the 4f electrons in 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 if more than one RE is incorporated, the RE ion's lattice location and/or coordination. Measurements of the g value from electron paramagnetic resonance experiments (EPR) [5, 6] as well as from Zeeman measurements [7] are able to distinguish between different RE

ions and for the same ion in different valence states. Ions with an odd number of electrons obey Kramers theorem and will have a different Hamiltonian from those with an even number of electrons. In a lattice site with cubic symmetry a spin 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 the 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 evidence of the identity of the ion, its valence as well as providing evidence of whether the ion is located at a substitutional or interstitial site. Despite being extensively employed [9–12], the average g value calculated from experiment may not correctly match the cubic g value predicted from theory. Specific examples of this taken from the literature will be given in section 2. This discrepancy between theory and experiment has led to a questioning of the validity and limits of 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.

The erbium system was chosen as there has been considerable research effort put in into understanding the properties of the Er^{3+} ion as the optical transition wavelength from the first spin orbit excited state to the ground state occurs at 1.5 μm . This is a technological important wavelength

since it matches the minimum in the dispersion of silica based optical fibres and has acted as the catalyst for the development of the erbium doped fibre amplifier and optical doping of materials [1, 2]. In relation to magnetic resonance measurements the fact that the first excited spin-orbit state is 6500 cm^{-1} above the ground state means that the effects of higher lying states can largely be ignored. Ignoring these interactions means it is easier to probe the properties of the ground state with greater confidence. As such erbium is an ideal ion to study as it is possible to make reliable calculations and compare them with extensive measurements. In this paper we begin with a study of the magnetic resonance properties of the Er^{3+} in cubic symmetry before examining the lower symmetry cases.

2. Trivalent erbium in a cubic crystal field

The magnetic resonance ground state properties of the Er^{3+} ion are largely determined by the eleven electrons located in the 4f shell. Contributions from other effects, such as the nuclear hyperfine interaction from the 23% abundant Er^{167} (with nuclear spin $I = 7/2$), can be treated within perturbation theory. The electron configuration of the eleven 4f electrons results in a spin quantum, S , of $3/2$ and an orbital quantum number, L , of 6. As the 4f shell is more than half full the total angular momentum quantum number, J , is $15/2$. This produces, in general, a 16-fold degenerate ${}^4\text{I}_{15/2}$ spin-orbit (SO) ground state level which is separated by about 6500 cm^{-1} from the 14-fold degenerate ${}^4\text{I}_{13/2}$ first excited SO state with $J = 13/2$. The important optical transition at $1.5 \mu\text{m}$ occurs between these two states. Other higher lying excited states such as those with $J = 11/2$ and $9/2$ exist as well as ${}^2\text{K}_{15/2}$ and ${}^2\text{L}_{15/2}$, however, in the remainder of this paper we will concentrate on the ${}^4\text{I}_{15/2}$ ground state and the effects of the host crystal field.

The incorporation of an Er^{3+} ion in a host semiconductor results in Stark splitting of the SO levels, the number and symmetry of which are determined by the symmetry of the crystal field. For all symmetries other than cubic, the 16-fold degenerate SO level splits into eight Kramers doublets. When the ion is incorporated into a cubic semiconductor with T_d symmetry, group theoretical arguments show that splits the 16-fold ground state SO level into five Stark distinct levels. These consist 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 these Stark levels is determined by the relative strength of the fourth and sixth order crystal field terms in the cubic crystal field Hamiltonian [8]

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

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

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

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 [13] and the values of β and γ depend upon L , S and J and have been tabulated elsewhere¹. Note that there are two conventions that are commonly used to make these types of calculations—the Stevens normalization convention, which is the one employed here and the Wybourne normalization convention. The two approaches use different constants and the interested reader is referred to section 2.2 of [13] for further information and the links between the two conventions.

In the seminal work by Lea *et al* [14] it was shown that solution to the Hamiltonian in equation (1) can be obtained using the substitutions

$$B_4 F_4 = Wx \quad (3a)$$

and

$$B_6 F_6 = W(1 - |x|), \quad (3b)$$

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 $F_6 = 13860$, see [14]. The parameter x is the crystal field mixing term related to the ratio of B_4 to B_6 and runs from -1 to $+1$. From equations (3a) and (3b) it is possible to calculate the value of x . For positive x this will be $x = \frac{B_4 F_4}{B_6 F_6 + B_4 F_4}$; for negative x there will be a minus sign in the denominator. The change of sign comes about due to the presence of the magnitude of x appearing in the equation (3b) above. 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 .

The values of $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$ depend on the lattice coordination of the RE ion. For example, for an Er^{3+} ion located at a substitutional site in a zincblende lattice the values of $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$ can be calculated from the equations [15]

$$A_4 \langle r^4 \rangle = \left(\frac{7}{36} \frac{Z_1 e^2}{R_1^5} + \frac{7}{32} \frac{Z_2 e^2}{R_2^5} \right) \langle r^4 \rangle \quad (4a)$$

and

$$A_6 \langle r^6 \rangle = \left(-\frac{1}{18} \frac{Z_1 e^2}{R_1^7} + \frac{3}{64} \frac{13}{4} \frac{Z_2 e^2}{R_2^7} \right) \langle r^6 \rangle \quad (4b)$$

where Z_1 and Z_2 are the charges of the neighbouring ions and values of $\langle r^4 \rangle$ and $\langle r^6 \rangle$ for Er^{3+} are given in [8, 16]. Employing equations (4a) and (4b) for an Er^{3+} ion at a Zn substitutional site surrounded by four Se^{2-} ions (with $Z_1 = -2$) located at a distance of R_1 away and twelve next nearest neighbour Zn^{2+} ions ($Z_2 = +2$) at R_2 away gives values of $A_4 \langle r^4 \rangle = -40.4 \text{ cm}^{-1}$ and $A_6 \langle r^6 \rangle = 2.29 \text{ cm}^{-1}$, respectively when $R_1 = \frac{\sqrt{3}a}{4}$ and $R_2 = \frac{a}{2}$, with a being the ZnSe lattice constant

¹ The multiplicative constants for Er^{3+} are $\alpha = 2.539 \times 10^{-3}$, $\beta = 4.44 \times 10^{-5}$ and $\gamma = 2.07 \times 10^{-6}$.

taken as 0.5668 nm. The corresponding values of x and W can be calculated to be -0.622 and 0.173 cm^{-1} . Note that at a substitutional site the effects of the twelve second shell next nearest neighbour (nnn) atoms has been included in the above calculation. The second shell of $\langle 110 \rangle$ oriented atoms is located 1.633 times further out than the first shell of four $\langle 111 \rangle$ oriented atoms and sometimes in the literature the contribution of the second shell for a substitutional site is ignored. In such a situation the values of $A_4\langle r^4 \rangle = -44.7 \text{ cm}^{-1}$ and $A_6\langle r^6 \rangle = 2.10 \text{ cm}^{-1}$ with the corresponding values of x and W are -0.664 and 0.179 cm^{-1} . Similar equations [15] for interstitial sites can also be written however, as the six nnn atoms which are in $\langle 100 \rangle$ directions are only 15% further out from the nn shell of atoms, it is essential to include the effects of the second shell. Using a similar notation to equation (4) (we denote an interstitial site with a star) the equations take the form

$$A_4^*\langle r^4 \rangle = \left(\frac{7}{36} \frac{Z_1 e^2}{R_1^5} - \frac{7}{16} \frac{Z_2 e^2}{R_2^5} \right) \langle r^4 \rangle \quad (5a)$$

and

$$A_6^*\langle r^6 \rangle = \left(-\frac{1}{18} \frac{Z_1 e^2}{R_1^7} - \frac{3}{64} \frac{Z_2 e^2}{R_2^7} \right) \langle r^6 \rangle. \quad (5b)$$

Values of $A_4^*\langle r^4 \rangle = 93.8 \text{ cm}^{-1}$ and $A_6^*\langle r^6 \rangle = -1.45 \text{ cm}^{-1}$ can be calculated for an Er^{3+} ion located at a interstitial site surrounded by four Zn^{2+} ions and six Se^{2-} ions. The corresponding values of x and W are -0.85 and -0.29 cm^{-1} , respectively. These examples show how the value of x can distinguish between a substitutional site and an interstitial site reflecting the different arrangement of the cations and anions. Note the value of x reflects the ratio of B_4/B_6 and as such the choice of formal charges (Z_1 and Z_2) 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 can be employed. In general, the crystal field eigenstates $|\psi\rangle$, and the time reversed state $|\psi'\rangle$, are a normalized superposition of the $|m_J\rangle$ states associated with the quantum number J with the values of m_J running from $-J$ to $+J$ and are given by

$$\begin{aligned} |\psi\rangle &= \sum_m c_m |m_J\rangle \quad \text{and} \\ |\psi'\rangle &= \sum_m (-1)^{J-m} c_m^* | -m_J \rangle \end{aligned} \quad (6)$$

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

$$\begin{aligned} \Gamma_6: & 0.6332|\pm 13/2\rangle + 0.5819|\pm 5/2\rangle \\ & - 0.4507|\mp 3/2\rangle - 0.2393|\mp 11/2\rangle \end{aligned} \quad (7a)$$

and

$$\begin{aligned} \Gamma_7: & 0.5818|\pm 15/2\rangle + 0.3307|\pm 7/2\rangle \\ & + 0.7182|\mp 1/2\rangle + 0.1910|\mp 9/2\rangle. \end{aligned} \quad (7b)$$

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 equations (7a) and (7b) 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 $|m_J\rangle$ states in equations (7a) and (7b) 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 state 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 state when $-0.46 < x < 0.58$. This independence of the g value for both the Γ_6 and Γ_7 states with x 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 conventionally 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. As noted earlier, results from experiments may not always match with the results from the theory described above. For example, recently Vinh *et al.*, on the basis of Zeeman measurements made on an Er doped Si MBE multilayer structure, reported an Er^{3+} centre (labelled L_1^1) with an average g value of 6.1 ± 0.5 which they attributed to a Γ_6 state [10]. Dziesiaty *et al* in their study of erbium centres in ZnSe reported the presence of both Er^{3+} and Er^{2+} centres [11]. For the case of one of the Er^{3+} centres (labelled centre A) g values of $g_1 < 0.57$ (along the $\langle 111 \rangle$ direction), $g_2 = 8.88$ (along $\langle 110 \rangle$ direction) and $g_3 = 12.03$ (along $\langle 112 \rangle$ direction) were reported which they interpreted as implying that this centre was approximately axial with respect to the $\langle 111 \rangle$ direction with g_{\parallel} less than 0.5 and g_{\perp} taken as $g_{av} = 1/2(g_2 + g_3) = 10.5$. Employing this strategy gives an average g value of 6.97 which from they conclude that centre A derives from a Γ_6 state even though this is above the predicted value of 6.8. Watts and Holton [17] reported some axial spectra associated with an Er^{3+} in hexagonal ZnS with an average g value of 6.665 and a centre in CdS with an average g value of 6.426. Both of these centres were attributed to a Γ_6 ground state. The solid lines in figure 1 show how the principal g values must vary for a centre with an average g value of 6.0 and 6.8 along with some reported values from the literature. Figure 1 shows that from a range of samples the calculated average values appear to follow the pattern predicted by the CCF approximation. However, there is a greater tendency for more data points to lie on the line associated with the Γ_6 state,

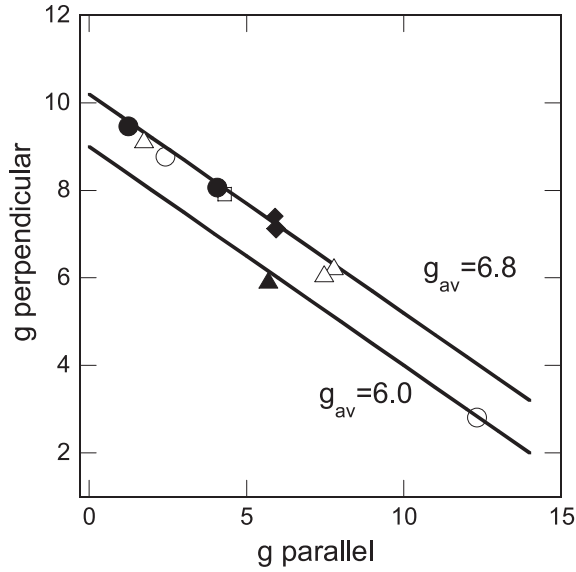


Figure 1. Solid lines show the variation of g_{\perp} with g_{\parallel} for Er^{3+} with g_{av} equal to 6.0 or 6.8. Symbols are experimentally measured values in a range of hosts: (●) ZnTe data from [12]; (○) ZnS from [17], (□) CdTe from [12]; (▲) InP from [5], (◆) BaF_2 from [5] and (△) CaF_2 from [21].

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 explicitly calculated the g values as a function of axial crystal field strength.

3. 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 equation (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

$$H_{\text{tetra}} = B_2O_2^0 + B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4), \quad (8)$$

with $B_2 = \alpha A_2 \langle r^2 \rangle$ as before [8] (see footnote 1). Numerical diagonalization of equation (8) gives for a Γ_7 crystal field eigenstate of the form

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

The principal g values are given by

$$\begin{aligned} g_{\parallel} &= 2g_J \langle \psi | J_z | \psi \rangle & \text{and} \\ g_{\perp} &= g_J \langle \psi' | J_+ + J_- | \psi \rangle, \end{aligned} \quad (10)$$

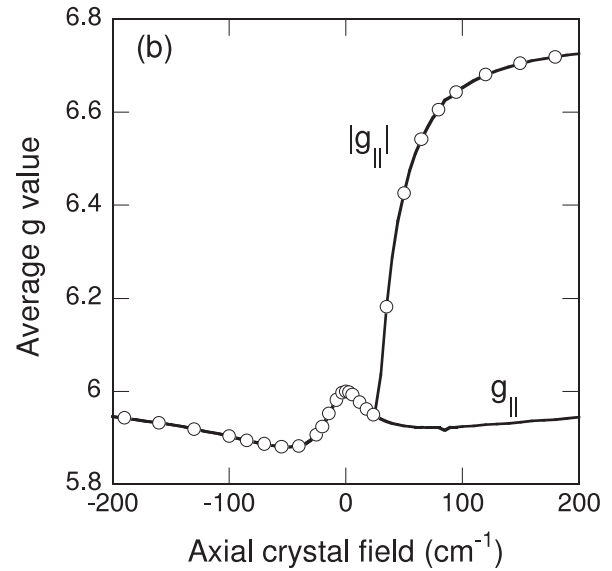
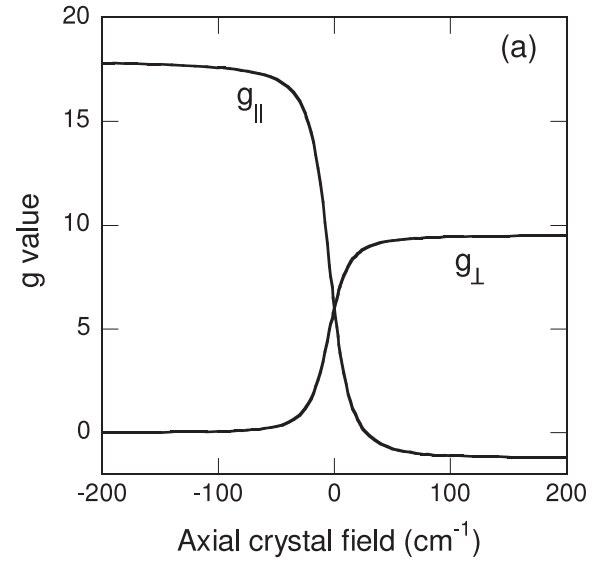


Figure 2. (a) Variation of principal g values g_{\parallel} and g_{\perp} as a function of axial crystal field for a state originating with a Γ_7 cubic ground state. (b) The average of the trace of g tensor, g_{av} , as calculated from (a) using the correct value and absolute value of g_{\parallel} .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

where the coefficients a_1-d_1 now depend on the value of the axial crystal field B_2 . Application of the ladder operators in equation (10) to the wavefunction in equation (9) gives the following expressions for the principal g values

$$g_{\parallel,1} = g_J(15a_1^2 + 7b_1^2 - c_1^2 - 9d_1^2) \quad (11a)$$

and

$$|g_{\perp,1}| = 2g_J(\sqrt{48}b_1d_1 + 4c_1^2). \quad (11b)$$

The variation of the principal g values calculated for a Γ_7 ground state over different axial crystal fields using equations (11a) and (11b) is shown in figure 2(a). 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 even with 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 observed. 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 2(a); 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 2(b) where the average g value calculated using the both the correct (i.e. negative) and absolute values of g_{\parallel} found in figure 2(a) 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 and 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 levelling 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 $g_{\text{av}} \sim 6.7\text{--}6.8$ 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 [17, 18] or crystal field mixing of higher lying states [13]. 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 [17, 18], usually expressed as $(1 - k)$ as

$$g'_J = g_J - (1 - k) \frac{J(J + 1) - S(S + 1) + L(L + 1)}{2J(J + 1)}. \quad (12)$$

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 [18]. 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 [19]). 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. For example the crystal field could mix in the Γ_7 level originating from the ${}^4I_{13/2}$ excited with the Γ_7 level in

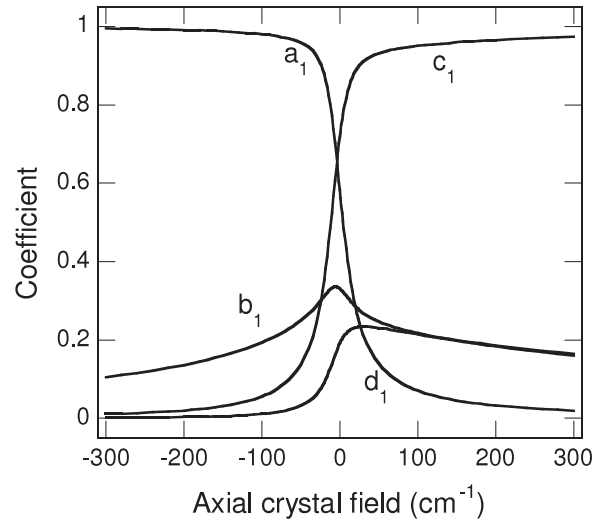


Figure 3. Variation of the coefficients a_1 to d_1 for a Γ_7 ground state as a function of axial crystal field. Note the rapid variation of a_1 with crystal field and the similar rapid change of g_{\parallel} in figure 2(a).

the ${}^4I_{15/2}$ ground state. Kingsley and Aven [20] suggested that the g value associated with the Γ_7 level in the presence of this crystal field mixing takes the form

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

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 equation (9) varies with axial crystal field (figure 3). It is apparent that the largest variation amongst the coefficients occurs for a_1 and c_1 with both b_1 and d_1 having a much smaller contribution. From equation (11a) 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 2(a) and the coefficient a_1 in figure 3. In the case of g_{\perp} , inspection of equation (11b) 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 $b_1 d_1$. 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

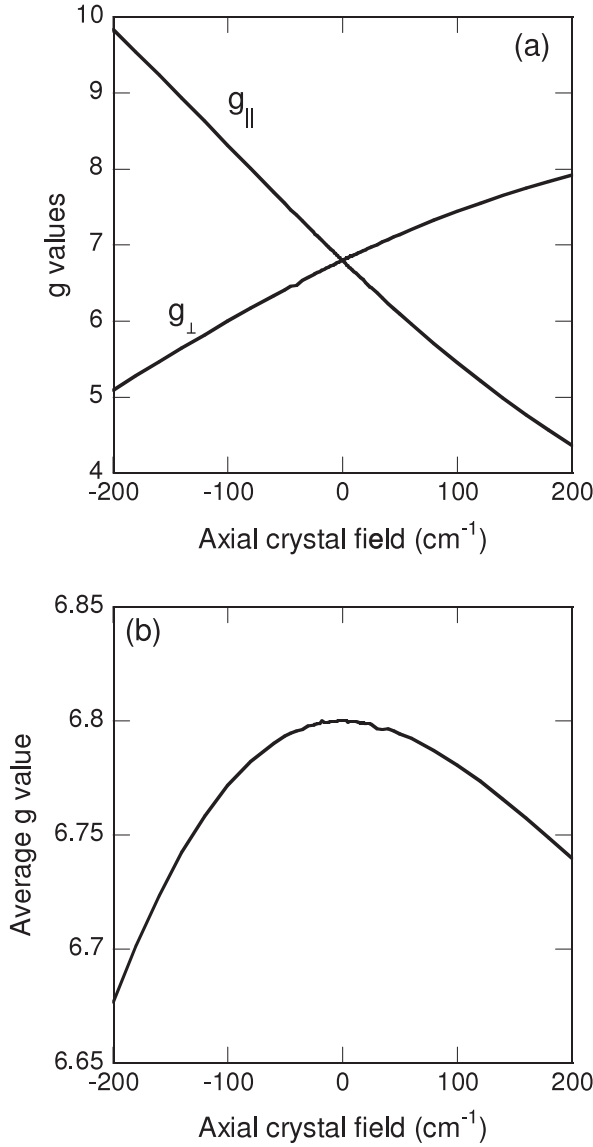


Figure 4. (a) Variation of principal g values $g_{\parallel,2}$ and $g_{\perp,2}$ as a function of axial crystal field for a state originating with a Γ_6 cubic ground state. (b) The average of the trace of g tensor, g_{av} .

are now mainly controlled by the $|\mp 1/2\rangle$ component of the overall crystal field eigenstates. We believe that it is this state 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 [21]. 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 wavefunction in terms of coefficients and the corresponding g values should satisfy the

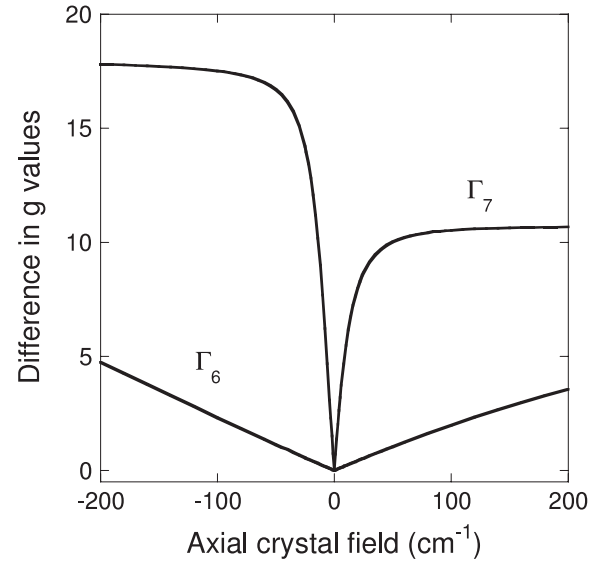


Figure 5. Variation of the difference in g values $|g_{\parallel} - g_{\perp}|$ for the both the Γ_7 and Γ_6 states. In the case of the Γ_6 state the difference in g values has a slope of $0.02/\text{cm}^{-1}$ which can then be used as a measure of the strength of the axial crystal field.

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 wavefunction derived from a Γ_6 state in an axial field can be expressed as

$$|\psi_2\rangle = a_2|13/2\rangle + b_2|5/2\rangle + c_2|-3/2\rangle + d_2|-11/2\rangle. \quad (14)$$

The principal g values in this case are

$$g_{\parallel,2} = g_J(13a_2^2 + 5b_2^2 - 3c_2^2 - 11d_2^2) \quad (15a)$$

and

$$|g_{\perp,2}| = 2g_J(\sqrt{28}a_2d_2 + \sqrt{60}b_2c_2). \quad (15b)$$

The variation of these g values (figure 4(a)) and average g value (figure 4(b)) 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). Furthermore over the course of $\pm 200 \text{ cm}^{-1}$ variation in the axial crystal 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 $0.02/\text{cm}^{-1}$, see 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.

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

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

The presence of O_n^3 terms ensures that the highest m -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 $|m_J\rangle$ that appear in the wavefunction expansion will differ by 3. For the Γ_7 state in trigonal symmetry the wavefunction is

$$|\psi_3\rangle = a_3|15/2\rangle + b_3|9/2\rangle + c_3|3/2\rangle + d_3|-3/2\rangle + e_3|-9/2\rangle + f_3|-15/2\rangle. \quad (17)$$

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 $|m_J\rangle$ 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

$$|\psi_4\rangle = a_4|13/2\rangle + b_4|7/2\rangle + c_4|1/2\rangle + d_4|-5/2\rangle + e_4|-11/2\rangle, \quad (18a)$$

and we calculate that the corresponding principal g values will be

$$g_{\parallel,4} = g_J(13a_4^2 + 7b_4^2 - c_4^2 - 5d_4^2 - 11e_4^2) \quad \text{and} \quad (18b)$$

$$|g_{\perp,4}| = 2g_J(-\sqrt{28}a_4e_4 + \sqrt{55}b_4d_4 - 4c_4^2).$$

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

The above analysis has been performed for the Er^{3+} ion but can be extended to other ions. While not reviewing the magnetic resonance properties of the whole of the RE ion series it is worth immediately noting that both Tm^{4+} and Ho^{2+} ion are isoelectronic with the Er^{3+} ion. This means that they share all the same quantum numbers and Landé g value. As a result the analysis of the EPR measurements of these ions which show axial spectra will need to take into account the results discussed above. In addition the Dy^{3+} ion possesses nine 4f electrons which gives it a ${}^6\text{H}_{15/2}$ ground state ($S = 5/2$ and $L = 5$). The composition of wavefunctions for the various Stark levels will be the same as those in equations (7a) and (7b). Only the Landé g value will be different being 4/3 for Dy^{3+} when compared with 6/5 for Er^{3+} . This means that the matrix elements that are employed to calculate the cubic g value will be the same and we can immediately calculate that the g value associated with a Γ_6 level will have a value of 7.55 while that of Γ_7 level will be 6.66. In axial symmetry the same wavefunction expansion as those used in equations (9) and (14) will be used. Once again the conclusions obtained here are relevant to this ion. Only by exact calculation for the others ions is it possible to determine if state mixing is a significant effect. One simple test would be to examine the matrix elements associated with how the O_2^0 crystal field operator transforms for each value of J .

4. 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 $|m_J\rangle$ in the wavefunction. We believe that balanced wavefunctions obey the CCF approximation and using circularly polarized radiation is able to resolve any ambiguity.

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