Lattice Location of Rare Earth Ions in Semiconductors: Interpretation and Limitations of using g values

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ABSTRACT

The g values of rare earth ions obtained from either paramagnetic resonance or Zeeman measurements are often used to interpret the location and/or environment surrounding rare earth ions. In the case of centres with cubic symmetry the g value can be used to distinguish between substitutional and interstitial sites. For centres with less than cubic symmetry the average g value, taken as 1/3 trace of the g tensor, is often used as an indication of the lattice location and/or a measure of the strength of the local crystal field. This approach is widely used but is based on the assumption that the non-cubic terms in the total crystal field potential are small compared with the cubic crystal field. In this paper we have explored this assumption by calculating the principal g values in axial crystal fields for the Er^{3+} ion. We examine the limits over which the average g value approach is valid. Comparison is made with published results.

INTRODUCTION

Light emission from rare earth (RE) ions is now well established with emission from Er^{3+} ions being of particular importance since the transition between the two lowest spin-orbit energy levels occurs at the technologically important wavelength of 1.55 μm . Efficient luminescence can be assisted by maximising the concentration of optically active centres. It is now generally established that this is not the same as maximising the RE ion concentration since precipitation and/or up-conversion effects can dominate at higher RE ion concentrations [1]. Incorporation of light atoms, such as oxygen and carbon, have been shown to increase the solubility limit of Er in silicon through the formation of erbium impurity complexes [2]. The most appropriate method that can be used to elucidate the lattice location of the *optically active* RE ion is a crystal field analysis of high resolution photoluminescence (PL) spectra. In addition, the lattice location and/or coordination of RE ions (which includes both optically active and inactive ions) can be obtained from extended X-ray absorption fine structure [3], Zeeman measurements [4] and electron paramagnetic resonance measurements (EPR) [5]. The results from the latter two experiments are usually discussed in terms of g values. In the case of Zeeman measurements, g values are extracted on the basis of fitting PL peak positions to a suitable spin Hamiltonian. For EPR, the variation of the resonance magnetic field, as a function of orientation between the Zeeman applied field and the crystal axes is measured. Again by fitting the observed variation to a spin Hamiltonian, g values can be obtained which in turn can be interpreted. For systems with less than cubic symmetry various approaches and simplifications are used. It is the aim of this paper to test some of the commonly used approaches to determine the applicability and limitations used for the case of Er^{3+} ions in zincblende hosts.

RESULTS AND DISCUSSION

Cubic crystal field approximation

The Er^{3+} ion possesses eleven $4f$ electrons which results in the lowest two spin-orbit ground states being $^4\text{I}_{15/2}$ (ground state) and $^4\text{I}_{13/2}$ (first excited state). Although the $4f$ electrons are shielded from the full interaction of the host crystal field, the spin-orbit levels are nevertheless split into Stark levels, the number and symmetry of which are determined by the symmetry of the crystal field. In the case of cubic symmetry, group theory shows that the 16-fold degenerate $^4\text{I}_{15/2}$ levels splits into five Stark levels labelled by the irreducible representations of the cubic group as $\Gamma_6 + \Gamma_7 + 3\Gamma_8$. Both Γ_6 and Γ_7 are doublets and each of the three Γ_8 are quartets. In the case of the $^4\text{I}_{13/2}$ state, a similar group theory analysis results in $2\Gamma_6 + \Gamma_7 + 2\Gamma_8$. Which of the energy levels lies lowest is determined by the exact coordination and usually expressed in terms of the crystal field Hamiltonian given in Eq. (1) below

$$H = B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4) \quad (1)$$

where O_m^n are the Steven's equivalent symmetry operators and B_4 and B_6 are the fourth and sixth order crystal field potentials, respectively. The solution to Eq. (1) is usually calculated by expressing the Hamiltonian in terms of a dimensionless variable x (a measure of B_4/B_6) which runs between -1 and +1 and energy scale parameter W . For the $^4\text{I}_{15/2}$ level, and with labelling appropriate to T_d symmetry, with $W > 0$, the Γ_7 level will lie lowest between $-1 < x < -0.46$, 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 spacing between the energy levels is controlled by W .

From the diagonalisation of the Hamiltonian in Eq. (1), the resultant crystal field eigenstates can be used to calculate the principal g values. For the case of the Γ_6 state the g value is 6.8 and for Γ_7 state the g value is 6.0. In both cases the g value is independent of x . The case of the lowest lying Γ_8 state is slightly more complicated, not because the spin Hamiltonian for a quartet is especially difficult, though additional terms may be need to be included, but the g value is now dependent on the value of x . Such a situation arises when the irreducible representation of the same symmetry appears more than once. The interpretation given to the value of x is also an important consideration. For the case of Er^{3+} ion in zincblende lattice, positive values of x are interpreted as implying that the RE ion is located at a tetrahedral interstitial site (T_i). Negative values of x suggest that the ion is located at a substitutional site (T_s). Such interpretations are based on knowledge of both the nearest neighbour (nn) and next nearest neighbour (nnn) atoms. In both T_i and T_s sites the nn atoms lie $\sqrt{3}a/4$ from the RE ion in equivalent $\langle 111 \rangle$ directions, however, in the T_s site the 12 nnn atoms lying in $\langle 110 \rangle$ directions are at a distance of $a/\sqrt{2}$, (a being the lattice constant). 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 nnn atoms that results in the positive value of x .

For the case of Er^{3+} centres with less than cubic symmetry, analysis of the g values is usually performed by examination of the average of the trace of the g value tensor, g_{av} , with the g values found in cubic symmetry where g_{av} is

$$g_{av} = 1/3(g_1 + g_2 + g_3) \quad (2)$$

This analysis is performed assuming that the total crystal field is dominated by the ‘parent’ cubic potential. The lower symmetry crystal field terms can then be considered as a perturbation to the cubic terms. In general, the average g value is often found to be slightly less than predicted for a Γ_6 or Γ_7 state. Such deviations are usually attributed to covalency effects and quantified using the orbital reduction factor $(1-k)$. Values of $(1-k)$ for different ions are given in table 1 below.

Table 1. Value of orbital reduction factor for a variety of hosts

Ion and Host	$(1-k)$	Ref.
Er^{3+} in $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$	0.02	6
Yb^{3+} in CaO	0.02	7
Tm^{2+} in CaF_2	0.01	7
Fe^{3+} in MgO	0.20	7
Ti^{3+} in Al_2O_3	0.30	7
Er^{3+} in Si	0.12	5

It is clear from the first three rows of Table 1 that the orbital reduction factors (ORFs) for RE ions are small (<0.03) but that significantly larger ORFs are found with ions from the first row of the transition series where crystal field effects are stronger. The final value of $(1-k)$ for the case of Er codoped with O in Si is the value that *would be* required to explain the average g value ($=6.28$) obtained from low temperature EPR measurements [5] if the corresponding cubic energy level has a g value of 6.8. Such a large ORF is not considered realistic for RE ions and large observed shifts away from predicted g values cannot be explained solely by covalency effects.

For the case of Er^{3+} in axial symmetry, both the Γ_6 and Γ_7 cubic levels remain as doublets and the cubic Γ_8 levels each split into two doublets. For the case of a small axial trigonal crystal field superimposed on the cubic field, variation of the principal g values $g_{\parallel}$ and $g_{\perp}$ can be seen in Fig. 1 below. Two sets of data are presented corresponding to two of three possible Γ_8 lying as the ground state.

Figure 1 Variation of $g_{\parallel}$ (open symbols) and $g_{\perp}$ (closed) in a trigonal crystal field. Squares correspond to a Γ_8 level lying lowest with $W < 0$ and circles for a Γ_8 level lying lowest with $W > 0$.

For the case of axial Er^{3+} centres derived from Γ_6 or Γ_7 states, the average g value should be equal to 6.8 or 6.0, respectively. The solid lines in Fig. 2 shows how $g_{\parallel}$ and $g_{\perp}$ must vary in order to satisfy this condition. Also included in Fig. 2 are g values for a number of Er^{3+} centres taken from the literature [8].

Figure 2 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 taken from the literature, summarised in reference 8, in a range of hosts.

Figure 2 shows that from a range of samples the predicted g values appear to follow the pattern expected by lying on either the line associated with Γ_6 or Γ_7 states. However, there is a greater tendency for more data points to lie on the line associated with Γ_6 state corresponding to an average g value of 6.8.

Non-cubic crystal field approximation

In order to test the validity of the predominantly cubic crystal field approximation as an explanation of the observed g value, an axial crystal field (of the form $B_2^0 O_2^0$) was superimposed on the Hamiltonian in Eq. (1). Shown in Fig. 3(a) below is the variation of the principal g values for a Γ_7 ground state over a wide range of axial crystal fields. It can first be observed that in the region where $g_{\parallel}$ (open circles) is high (above 10) the value of $g_{\perp}$ approaches zero. Indeed the value of $g_{\perp}$ is below 2 for $B_2^0 < -16 \text{ cm}^{-1}$. Since the intensity of the EPR transition is governed by the strength of the matrix element associated with $g_{\perp}$, these transitions will not normally be observable. We believe that this explains the sparse number of data points at high values of $g_{\parallel}$ in Fig. 2. For $B_2^0 < 30 \text{ cm}^{-1}$, the average g value is about 6.0 ± 0.1 , as observed in Fig. 3(b). Since $g_{\parallel}$ is less than zero when $B_2^0 > 30 \text{ cm}^{-1}$, Fig. 3(b) shows the average g value for both real (i.e. negative) and absolute values of $g_{\parallel}$. This is an important consideration since absolute value of $g_{\parallel}$ is usually measured in an experiment.

Figure 3 (a) Variation of $g_{\parallel}$ and $g_{\perp}$ for Er^{3+} assuming Γ_7 ground state. (b) Variation of average g value calculated from Fig. 3(a) assuming that the real (*i.e.* negative) value of $g_{\parallel}$ is used (solid line) or the absolute value of $g_{\parallel}$ is used (dashed line and closed symbols).

For $B_2^0 > 30 \text{ cm}^{-1}$, Fig. 3(b) shows that the average g value begins to deviate from that predicted by assuming the cubic crystal field dominates if the absolute value of $g_{\parallel}$ is used. For an axial field with $B_2^0 = 60 \text{ cm}^{-1}$, $g_{\text{av}} = 6.51$ and at high axial fields strengths ($\sim 150 \text{ cm}^{-1}$), g_{av} reaches 6.70 before leveling off. It is in this regime that it may appear that g value is now reminiscent of that associated with a Γ_6 state, rather than Γ_7 . When the real value is used in its place g_{av} stays within 0.1 of what would be predicted. As a result care must be employed when interpreting the average g value in this case.

Figure 4 (a) Variation of $g_{\parallel}$ and $g_{\perp}$ for Er^{3+} assuming Γ_6 ground state. (b) Variation of average g value calculated from Fig. 4(a).

No significant change of the principal g values is observed (Fig. 4(a)) for the Γ_6 ground state and as a result the average g value does not deviate significantly from 6.8 over the wide range of axial fields that have been used. 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 as shown in (Fig. 4(b)).

Finally, we note that for the Γ_6 state the magnitude of the g value difference, $|g_{\parallel} - g_{\perp}|$, scales approximately linearly with axial field up to 200 cm^{-1} with a slope of $0.02 / \text{cm}^{-1}$. As such the $|g_{\parallel} - g_{\perp}|$ may be used as a quantitative measure of the strength of the axial field. However, we do not find such a linear relationship for the Γ_7 state.

CONCLUSIONS

In this paper we have calculated the principal g values associated with an Er^{3+} centre with axial symmetry with different possible ground states. We have investigated the well known approach of using the average g value as an indication of the ground state. These results show that the use of the average g value is acceptable over a wide range of axial field strengths for a Stark level with a Γ_6 ground state. However, the approximation may lead to incorrect assumptions for a Γ_7 ground state in the presence of strong axial fields where the value of $g_{\parallel}$ is less than zero. As a consequence care must be considered if the correct assignment is Stark energy level is to be made. The effects of covalency have been discussed and any observed large difference between g_{av} and the g value predicted from cubic symmetry are unlikely to be due to covalency effects.

ACKNOWLEDGEMENTS

DC acknowledges the EPSRC for funding via an Advanced Research Fellowship.

REFERENCES

1. see, for example, MRS Proceedings on light emission from silicon.
2. F. Priolo, G. Franzò, S. Coffa, A. Polman, S. Libertino, R. C. Barklie and D. Carey, J. Appl. Phys. **78**, 3874 (1995).
3. A. Terrasi, G. Franzò, S. Coffa, F. Priolo, F. D'Acapito and S. Mobilio, Appl. Phys. Lett. **70** 1712 (1997)
4. N.Q. Vinh, H. Przybylinska, Z.F. Krasil'nik and T. Gregorkiewicz, Phys. Rev. Lett. **90**, 066401 (2003)
5. J. D. Carey, R. C. Barklie, J. F. Donegan, F. Priolo, G. Franzò and S. Coffa, Phys. Rev. **B 59**, 2773 (1999).
6. S.-Y. Wu and H.-N. Dong, J. Alloys and Compounds **379**, 36 (2004).
7. values quoted from A. Abragam and B. Bleaney *Electron Paramagnetic Resonance Ions* (Oxford: Oxford University Press, 1970)
8. C.A.J. Ammerlann and I. De Maat-Gersdorf, Appl. Magn. Reson. **21**, 13 (2001).