Solid State Phenomena Vols. 82-84 (2002) pp. 657-662

Spectroscopic Characterisation of Erbium Impurity in Crystalline Silicon

C.A.J. Ammerlaan and I. de Maat-Gersdorf

Van der Waals-Zeeman Institute, University of Amsterdam, Valckenierstraat 65,
NL-1018 XE Amsterdam, The Netherlands

Keywords: Energy Levels, Erbium, Magnetic Resonance, Optical Spectroscopy, Silicon

Abstract. A fully numerical scheme for the computation of energy levels and wave functions of rare-earth impurities in crystalline solid matrices has been developed. In this paper, application to the specific case of the erbium ion in semiconductors is taken as example. The lifting of spin–orbit degeneracy due to ligand fields of neighbouring host-crystal atoms in cubic, trigonal, tetragonal and orthorhombic co-ordination is quantitatively considered. Existing data for the well-identified luminescence spectra Si-Er-C, the main cubic spectrum, and of the low-symmetry centres Si-Er-1 and Si-Er-O1,2 are interpreted within the level diagram. Adding the Zeeman Hamiltonian, the *g* tensors for further splitting in a magnetic field, removing all degeneracy, were calculated. Principal *g* values for a recently reported centre Si-OEr-1 of monoclinic symmetry can be well explained by the calculations.

Introduction

Research by the methods of spectroscopy provides deep insight into the physical properties of electronic centres in solids, in fundamental terms. Observed transition energies in optical or magnetic resonance spectra allow the construction of the diagram of energy eigenvalues. Intensities reflect the transition probabilities, which depend on wave functions. Such basic information is relevant for the development of devices with optimum characteristics, e.g., in the area of light generation. In this paper, a numerical scheme for the computation of energy levels and wave functions of rare-earth impurities in crystalline solid matrices will be presented. To illustrate the method and results, application to the case of the erbium ion in semiconductors is taken as specific example.

Physical–Mathematical Basis

Spin–orbit interaction. For rare-earth ions the largest correction to be considered on the levels in the Coulomb electrostatic field, arises from spin–orbit interaction. With their incompletely filled 4f shell, rare-earth ions generally have large uncompensated spin and orbital momentum. For the Er^{3+} ion, with electron configuration $4f^{11}$, and following Hund's rule of level occupation, the orbital momentum is $L = 6$ and the electron spin is $S = 3/2$. By the spin–orbit interaction $\lambda\mathbf{L}\cdot\mathbf{S}$ these 52 degenerate states divide themselves over four levels with total angular momentum $J = L + S = 15/2$, $J = 13/2$, $J = 11/2$ and $J = L - S = 9/2$, respectively. For Er^{3+}, with a negative spin–orbit coupling constant λ, the state $^4I_{15/2}$ forms the ground state. It is separated from the next higher state $^4I_{13/2}$ by about 800 meV. Calculations presented in this paper are restricted to the isolated ground state with still 16-fold degeneracy using the spin J formalism. The Landé factor for splitting in a magnetic field is $g_J = 1 + [J(J + 1) - L(L + 1) + S(S + 1)]/2J(J + 1) = 6/5$.

Crystal field. When present as an impurity in a crystal, the erbium ion is subject to the fields exerted by surrounding host atoms, modifying energy levels and wave functions. In the crystal field the degeneracy of the spin–orbit levels is lifted, the precise effect depending on strength and symmetry of the crystal field. Calculations of the energy levels were performed for centres of cubic, trigonal, tetragonal and orthorhombic symmetry. The crystal potential is represented by its equivalent spin operator H_{cf}. A general expression for the crystal-field Hamiltonian has the form of the linear combination

Table 1. Energies of the luminescence spectra labelled Er-C, Er-1 and Er-O1,2 related to erbium in silicon. Observed luminescence transition energies E, excitation energies ΔE with respect to the lowest crystal-field level. All energies in cm^{-1}.

Spectrum	Er-C		Er-C		Er-C		Er-1		Er-O1,2	
Energies	E	ΔE	E	ΔE	E	ΔE	E	ΔE	E	ΔE
Spectral components	6504.1	0	6507.5	0	6504.8	0	6502	0	6508	0
	6426.7	77.4	6429.2	78.3	6426.0	78.8	6443	59	6472	36
	6349.2	154.9	6352.0	155.5	6348	157	6433	69	6438	70
	6259.8	244.3	6258.6	248.0	6256	249	6392	110	6385	123
	6097.6	406.5			6087	418	6342	160	6314	194
							6336	166	6229	279
							6268	234	6173	335
							6231	271		
Reference	3		4		5		6,7		5	
V_{cf}	0.654		0.654		0.654		0.438			
α [degree]	28		28		28		0			
β [degree]	0		0		0		12			
γ [degree]	0		0		0		0			

$$H_{\mathrm{cf}} = V_{\mathrm{cf}}(\cos\gamma . H_{\mathrm{cuax}} + \sin\gamma . H_{\mathrm{or}}), \tag{1}$$

with

$$H_{\mathrm{cuax}} = \cos\beta . H_{\mathrm{cu}} + \sin\beta . H_{\mathrm{ax}} \tag{2}$$

and

$$H_{\mathrm{cu}} = \cos\alpha . H_{\mathrm{cu6}} + \sin\alpha . H_{\mathrm{cu4}}, \tag{3}$$

with H_{cu4} and H_{cu6} representing the fourth- and sixth-order cubic operators O_4 and O_6, H_{ax} an axial operator for the trigonal or tetragonal field and H_{or} the low-symmetry operator of orthorhombic or monoclinic character. Explicit expressions for these operators are given in textbooks on the ligand field theory [1], or in ref. [2]. Whereas V_{cf} determines the total strength of crystal-field energies, the relative contributions of distinct symmetries are specified by the parameters α, β and γ. As a result of the ligand field, in a high-symmetry cubic surrounding the ground state $^4I_{15/2}$ will split into three quartets of Γ_8 character and two doublets, one for each of the Γ_6 and Γ_7 representations. For a low-symmetry field, the maximum number of eight Kramers doublets will be obtained. Crystal-field induced splittings are of order of magnitude 50 meV.

Magnetic field. To account for the effect of a magnetic field, the operator representing the Zeeman energy

$$H_{\mathrm{mf}} = g_J \mathbf{B} \cdot \mathbf{J} \tag{4}$$

with $|\mathbf{B}| = 1$ is added to operator H_{cf} of the crystal field. By the Zeeman effect the degeneracy in the crystal-field quartet and Kramers doublet levels is lifted. In the regime of weak magnetic field the

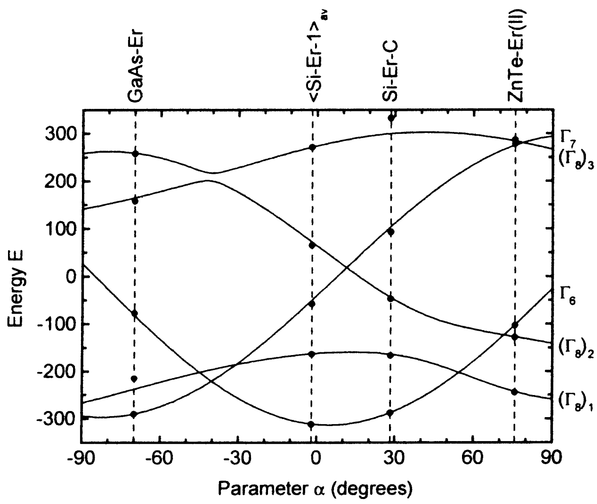

Figure 1. Crystal-field energies of the doublets Γ_6 and Γ_7 and of quartet levels $(\Gamma_8)_i$, i = 1, 2 and 3, of the Er^{3+} ion in a crystal field of cubic symmetry. Eigenvalues of the set of equation (1) to (3) calculated for V_{cf} = = +1 and with parameter α controlling the mixing of fourth- and sixth-order cubic potentials. Data points (•) taken from refs 5, 7, 9 and 10 include the averaged spectrum $<$Si-Er-1$>_{av}$.

induced level splittings are proportional to the field and hence characterised by constant effective g values. From the calculated splittings, which in general depend on orientation of magnetic field, the g tensors are derived. For an electron paramagnetic resonance (EPR) experiment performed in the K band, i.e., at around the microwave frequency of 23 GHz, a Zeeman splitting of about 0.1 meV is in most cases small compared to the separation of states formed after spin–orbit and crystal-field interactions. To ensure such conditions in the calculations, in the total spin Hamiltonian $H_{cf} + H_{mf}$ the coefficient V_{cf} for the strength of crystal field was usually given a value $V_{cf} = 1000$. It may be noted, however, that 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 treated without modification. Calculations have included centres from high cubic symmetry in Γ_6 or Γ_7 states with isotropic EPR spectra and scalar g values, cubic-symmetry centres in Γ_8 states requiring effective spin $J = 3/2$ and a Hamiltonian with a third-order spin operator, 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.

Photoluminescence

In photoluminescence experiments the observed emissions correspond to transitions from the $^4I_{13/2}$ first excited spin–orbit level to the lowest level $^4I_{15/2}$. The multi-line structure in the spectrum reveals the crystal-field effect in the spin–orbit ground state. In Table 1 energies E of the components are listed for the spectra Si-Er-C [3,4,5], Si-Er-1 [6,7] and Si-Er-O1,2 [5]. From the differences the crystal-field energies ΔE are derived. Energies reported for the five lines of the cubic centre Er-C in different literature sources agree quite well. A calculated energy level diagram, as presented in Figure 1, shows the energies for $V_{cf} = +1$ as a function of parameter α describing the mixture of 4th- and 6th-order cubic crystal-field energies. The diagram is equivalent to the well-known diagrams based on the treatment of Lea, Leask and Wolf [8]. The spectrum of the cubic

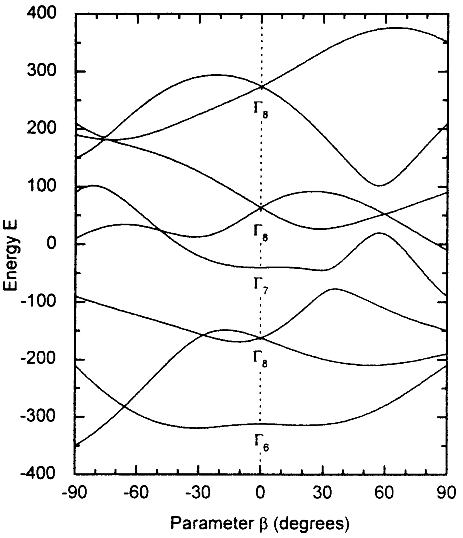

Figure 2. Energies of eight doublets for a sixth-order cubic crystal field, $\alpha = 0^\circ$, together with a second-order trigonal crystal field, calculated by Equations (1) to (3) with $V_{cf} = +1$ and parameter β in the range $-90^\circ \leq \beta \leq +90^\circ$ controlling the mixing of the cubic and trigonal fields.

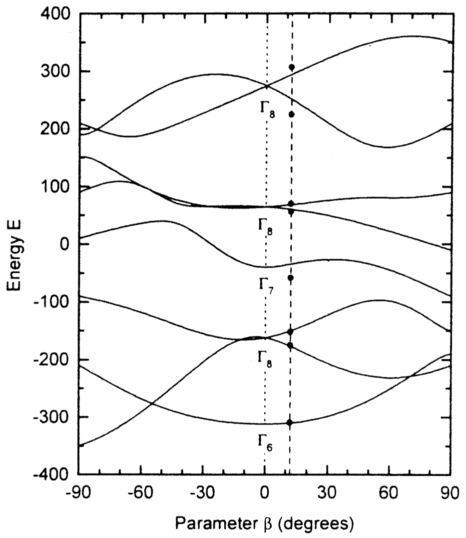

Figure 3. Energies of eight doublets for a sixth-order cubic crystal field, $\alpha = 0^\circ$, together with a second-order tetragonal crystal field, calculated by Equations (1) to (3) with $V_{cf} = +1$ and parameter β in the range $-90^\circ \leq \beta \leq +90^\circ$ controlling the mixing of the cubic and tetragonal fields.

centre is well fitted by parameters $V_{cf} = 0.654$ cm^{-1} and $\alpha = +28^\circ$. For some extra perspective the interpretation of spectra of erbium in the semiconductors GaAs and ZnTe is also indicated in the figure [9,10].

The eight-line spectrum Si-Er-1 must correspond to a centre of lower-than-cubic symmetry. On inspecting the structure of the spectrum it appears that three pairs of close-lying lines can be distinguished, at 59 and 69, at 160 and 166, and at 234 and 271 cm^{-1}, respectively. It may be speculated that these groups are formed by a relatively small splitting of a quartet Γ_8 state in a field of near-cubic symmetry. The ordering of levels, from low to high energy, in the cubic approximation is doublet, quartet, doublet, quartet, quartet. As can be observed in figure 1, such ordering exists for $V_{cf} > 0$ and parameter α in the range $-30^\circ < \alpha < +10^\circ$. Averaging the energies of the pair lines, one obtains an artificial cubic five-line spectrum with the energies at 0, 64, 110, 163 and 252 cm^{-1}. As shown in figure 1, this spectrum can be well adjusted into the cubic level diagram for a value $\alpha = -2^\circ$. Splitting of the three quartet states into two doublets each in a field of lower symmetry will give the full eight-line spectrum. Such splitting is shown as calculated for axial trigonal or tetragonal fields in the figures 2 and 3, respectively. The figures are for $\alpha = 0^\circ$ and with parameter β covering the full range $-90^\circ \leq \beta \leq +90^\circ$ of mixing cubic and axial fields. A good fit is found for the case of small tetragonal distortion specified by $\beta = 12^\circ$. Trigonal distortion does not offer a comparable solution. A similar treatment can be given to the spectra Si-Er-O1 and O2. The agreement reached is, however, less unambiguous and convincing. Probably, the spectra arise from centres with a symmetry lower than axial, requiring orthorhombic or monoclinic potentials to be included.

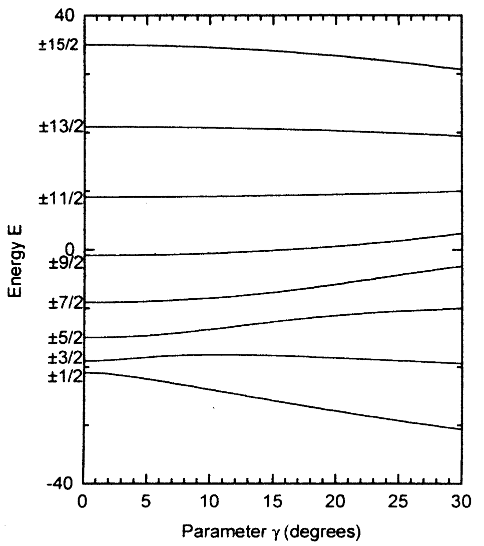

Figure 4. Energies of eight doublet levels in a combined tetragonal and orthorhombic crystal field. Parameters $V_{\mathrm{cf}} = +1$, $\beta = +90^\circ$, $-90^\circ \le \gamma \le +90^\circ$.

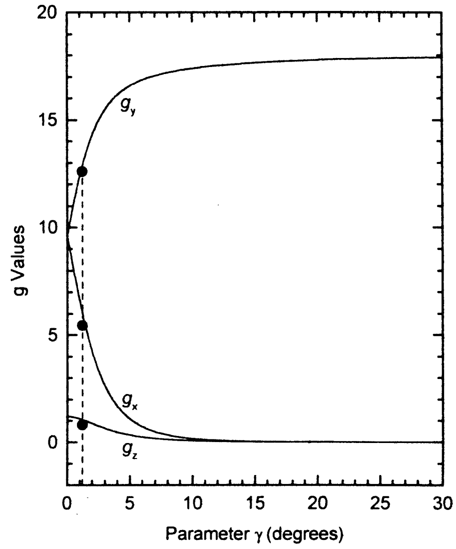

Figure 5. Zeeman splitting factors g_x, g_y and g_z for a paramagnetic centre in orthorhombic symmetry. Experimental data points (●) are for spectrum Si-OEr-1 [12].

Magnetic Resonance

With parameters known from optical spectra, the levels are characterised as regards their energies and wave functions. A splitting in an external magnetic field can be calculated in a straightforward manner applying Equation (4). This allows the prediction of g tensors as measured in magnetic resonance, which under normal conditions is observed for the lowest crystal-field level of the $^4\mathrm{I}_{15/2}$ spin–orbit state. For example, the GaAs:Er centre shown in figure 1 with α value near -70° is in a Γ_7 state and has an isotropic g value $g = 6$. The centre ZnTe:Er(II), with $\alpha = +76^\circ$, is in a quartet Γ_8 state and has an anisotropic behaviour to be described with effective spin $J = 3/2$. These conclusions are confirmed by actual experiments [10,11]. For the Si-Er-C centre, with $\alpha = +28^\circ$, the ground state level is expected to be of Γ_6 type with isotropic $g = 6.8$. The EPR spectrum has not yet been reported. The optical centre Si-Er-1 with crystal-field parameters $\alpha \approx 0^\circ$ and $\beta \approx +12^\circ$ will have an axial g tensor in tetragonal orientations. Principal g values for this centre are calculated to be $g_{//} \approx 4$ and $g_\perp \approx 7.5$ [2]. The values depend, however, in a sensitive manner on the distortion parameter β and are therefore better determined directly in a resonance experiment. A recently reported EPR spectrum corresponds to an erbium-related centre with a monoclinic-I symmetry [12]. The g tensor has the principal values $g_1 = 0.80$, $g_2 = 5.45$ and $g_3 = 12.60$, with the g_2 axis parallel to a <110> direction. Although hyperfine interaction revealing presence of the ^{167}Er isotope with the nuclear spin $I = 7/2$ was not detectable, strong indications for erbium involvement are the large anisotropy and the value 18.85 of the trace of the g tensor. To explore the properties of such low-symmetry centres a crystal field was considered in which in addition to a tetragonal axial field, as found for optical spectrum Si-Er-1, an orthorhombic field was included. By taking parameter β equal to $+90^\circ$ a cubic component was left outside consideration. Energy levels as calculated for this case are given as a function of parameter γ in figure 4, labelled with the m_J quantum numbers valid for axial symmetry. Levels do not cross, implying that either the $m_J = \pm 1/2$ or $m_J = \pm 15/2$ level is always the ground state. Most likely the $m_J = \pm 1/2$ level corresponding to positive V_{cf} constitutes the ground state; besides, a resonance in the $m_J = \pm 15/2$ state would be difficult to observe. Calculated principal g values for the ground state are shown in figure 5. A good agreement with the experimental values exists for distortion parameter $\gamma = 1.2$. A similar analysis can be applied to the g tensors reported for low-symmetry erbium-related centres in silicon carbide [13].

Conclusions

A numerical method for the calculation of energy levels and wave functions of rare-earth impurities in crystals on sites of various symmetries has been described. The versatile tool allows experimental data from optical spectroscopy (absorption and emission spectra, magneto-optics, optical detection of magnetic resonance) and electron paramagnetic resonance spectra to be interpreted.

Acknowledgement

One of the authors (CAJA) expresses gratitude to M.V. Stepikhova for valuable discussions on the Si-Er-1 luminescence spectrum.

References

[1] A. Abragam and B. Bleaney: *Electron Paramagnetic Resonance of Transition Ions* (Clarendon Press, England, 1970).

[2] C.A.J. Ammerlaan and I. de Maat–Gersdorf: Appl. Magn. Res. (2001).

[3] Y.S. Tang, K.C. Heasman, W.P. Gillin and B.J. Sealy: Appl. Phys. Lett. Vol. 55 (1989), p. 432.

[4] J. Michel, L.C. Kimerling, J.L. Benton, D.J. Eaglesham, E.A. Fitzgerald, D.C. Jacobson, J.M. Poate, Y.-H. Xie and R.F. Ferrante: Mater. Sci. Forum Vol. 83-87 (1992), p. 653.

[5] H. Przybylinska, W. Jantsch, Yu. Suprun-Belevitch, M. Stepikhova, L. Palmetshofer, G. Hendorfer, A. Kozanecki, R.J. Wilson and B.J. Sealy: Phys. Rev. B Vol. 54 (1996), p. 2532.

[6] B.A. Andreev, A.Yu. Andreev, H. Ellmer, H. Hutter, Z.F. Krasil'nik, V.P. Kuznetsov, S. Lanzerstorfer, L. Palmetshofer, K. Piplits, R.A. Rubtsova, N.S. Sokolov, V.B. Shmagin, M.V. Stepikhova and E.A. Uskova: J. Cryst. Growth Vol. 201-202 (1999), p. 534.

[7] M.V. Stepikhova, B.A. Andreev, V.B. Shmagin, Z.F. Krasil'nik, V.P. Kuznetsov, V.G. Shengurov, S.P. Svetlov, W. Jantsch, L. Palmetshofer and H. Ellmer: Thin Solid Films Vol. 369 (2000), p. 426.

[8] K.R. Lea, M.J.M. Leask and W.P. Wolf: J. Phys. Chem. Solids Vol. 23 (1962), p.1381.

[9] F. Bantien, E. Bauser and J. Weber: J. Appl. Phys. Vol. 61 (1987), p. 2803.

[10] J.D. Kingsley and M. Aven: Phys. Rev. Vol. 155 (1967), p. 235.

[11] M. Baeumler, J. Schneider, F. Köhl and E. Tomzig: J. Phys. C: Solid State Phys. Vol. 20 (1987), p. L693.

[12] J.D. Carey, R.C. Barklie, J.F. Donegan, F. Priolo, G. Franzò and S. Coffa: Phys. Rev. B Vol. 59 (1999), p. 2773.

[13] P.G. Baranov, I.V. Ilyin and E.N. Mokhov: Solid State Commun. Vol. 103 (1997), p. 291.