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# Spectroscopic characterisation of the erbium impurity in crystalline semiconductors

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# Abstract

A scheme for the numerical calculation of energy levels of rare-earth ions in a crystalline solid is presented. Stark fields of cubic, trigonal, tetragonal, orthorhombic and monoclinic symmetry are considered. As examples, optical luminescence spectra of erbium in the semiconductors zinc selenide and silicon are analysed. Based on the optical characterisation, the g tensors for Zeeman splitting in an applied magnetic field are predicted for the crystal-field ground states of these centres.  $\bigcirc$  2001 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

Spectroscopy is a general powerful tool for the investigation of electronic and atomic structure of matter, including solids and electronic centres in solids related to defects or impurities. By spectroscopy, transition energies and probabilities, parameters which are directly linked to the description of materials in fundamental terms of quantum mechanics are measured. Modern spectrometers, with high sensitivity and energy resolution, are capable of providing an abundance of very precise experimental data. In order to have the full profit of measured data, the interpretation in terms of solutions of the eigenvalue equations must be given. Unfortunately, often the system description is very complex due to, e.g., low symmetry or high spin. In general, an exact analytical solution of equations is only possible in specific cases of high symmetry. Applying perturbation theory, the range of analytical solutions can be extended, but perturbation methods suffer from limited applicability and unsatisfactory accuracy as well. To circumvent these strong limitations, the alternative method of numerical solution can be applied. This paper

describes a scheme for the calculation of energy levels, and at the same time wave functions, of rare-earth impurities in crystalline solids. The method is outlined and illustrated by the examples of the erbium ion in the semiconductor crystals zinc selenide and silicon, with the zincblende and diamond structures, respectively. The ground state of the Er<sup>3+</sup> ion with electronic configuration 4f<sup>11</sup> and, hence, orbital momentum L = 6 and spin  $S = \frac{3}{2}$ , is formed by spin-orbit interaction as a  ${}^{4}I_{15/2}$  level. Calculations on this state are performed in the effective spin  $J = \frac{15}{2}$  formalism. When included in a solid, the 16-fold degeneracy of the atomic state is partially lifted by crystal fields of ligand atoms of the host crystal with the formation of quartet and doublet levels. Application of a magnetic field, also considered in this paper, will result in 16 non-degenerate states.

# 2. Crystal-field Hamiltonian

In several cases, the erbium ion occupies a site of high symmetry, e.g. an undistorted substitutional site or interstitial T site. For rare-earth ions with 4f orbitals the only non-vanishing matrix elements are due to fourthand sixth-order crystal-field operators. On the basis of a point-charge model, expressions for the potential are

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 Table 1

 Potentials representing the eight systems in the diamond crystal structure<sup>a</sup>

System	Potential					
	$\overline{x^2}$	$y^2$	<i>z</i> <sup>2</sup>	xy	yz	zx
Cubic						
Trigonal	_		_	$\delta$	$\delta$	$\delta$
Tetragonal		_	γ	_		_
Orthorhombic-I			γ	$\delta$		
Monoclinic-I		_	γ	$\delta$	3	3
Orthorhombic-II		β	γ	_	_	
Monoclinic-II		β	γ	$\delta$		
Triclinic		β	γ	$\delta$	3	ζ

<sup>a</sup> Normalised second-order operators are constructed in a way as demonstrated by Eq. (5).

derived as

$$V_4 = 35(x^4 + y^4 + z^4) - 21r^4 \tag{1}$$

and

$$V_6 = 231(x^6 + y^6 + z^6) - 315(x^4 + y^4 + z^4)r^2 + 90r^6.$$
 (2)

Following the rules of quantum mechanics, the potentials are transformed into effective crystal-field operators. These are the familiar expressions  $H_{cu4} = O_4^0 + 5O_4^4$  and  $H_{cu6} = O_6^0 - 21O_6^4$ . In case of lower



Fig. 1. Crystal-field energy levels in state  ${}^{4}I_{15/2}$  of ZnSe: Er<sup>3+</sup>. (c) Eight levels derived from the photoluminescence spectrum, (a) calculated levels in cubic symmetry with parameters  $V_{cf} = 0.323$ ,  $\alpha = -0.7^{\circ}$ , (b) averaged to five-line spectrum, and (d) calculated levels in monoclinic-I symmetry, parameters  $V_{cf} = 0.334$ ,  $\eta = 26.3^{\circ}$ ,  $\alpha = -2.7^{\circ}$ ,  $\gamma = 37.0^{\circ}$ ,  $\delta = 33.1^{\circ}$ .

symmetry, additional operators are required. For the diamond and related crystal structures eight different systems can be distinguished, ranging from high-symmetry cubic, via axial trigonal and tetragonal, towards orthorhombic and monoclinic, to the lowest-symmetry case of the triclinic system. Associated crystal-field potentials represented by their leading second-order term are listed in Table 1. Again, the expressions for potential are transformed into operators by forming symmetrised forms of corresponding operators. From these operators, the matrix elements are formed in the basis set of the 16 spin states  $|15/2, m_J\rangle$  of the erbium ion.

The more general expression as used in the analyses of cases to be presented is of the monoclinic-I form. It is given by

$$H_{\rm cf} = V_{\rm cf}(\cos\eta H_{\rm cu} + \sin\eta H_{\rm mo}]$$
(3)

with

$$H_{\rm cu} = \sin \alpha \, H_{\rm cu4} + \cos \alpha \, H_{\rm cu6} \tag{4}$$

and

$$H_{\rm mo} = \cos \gamma H_{zz} + \sin \gamma [\cos \delta H_{xy} + (1/2)\sqrt{2} \sin \delta (H_{yz} + H_{zx})].$$
(5)

The usual scaling factors, F(4) = 60, F(6) = 13860, etc. are included in the operator expressions. Parameters  $\eta$ ,



Fig. 2. Crystal-field energy levels in state  ${}^{4}I_{15/2}$  of the Si–Er-1 centre. (c) Eight levels derived from the photoluminescence spectrum, (a) calculated levels in cubic symmetry with parameters  $V_{\rm cf} = 0.430$ ,  $\alpha = -1.7^{\circ}$ , (b) averaged to five-line spectrum, and (d) calculated levels in orthorhombic-I symmetry, parameters  $V_{\rm cf} = 0.437$ ,  $\eta = 19.3^{\circ}$ ,  $\alpha = -2.0^{\circ}$ ,  $\gamma = 24.8^{\circ}$ ,  $\delta = 0^{\circ}$ .

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Fig. 3. Crystal-field energy levels *E* in state  ${}^{4}I_{15/2}$  of the noncubic ZnSe:  $Er^{3+}$  centre as a function of parameter  $\eta$  of tetragonal distortion,  $V_{cf} = 0.323$ ,  $\alpha = -0.7^{\circ}$ . Data points in averaged cubic symmetry are shown at  $\eta = 0^{\circ}$ . Best match to potential with tetragonal symmetry is at  $\eta = 19.7^{\circ}$ .

 $\alpha$ ,  $\gamma$  and  $\delta$ , in the range  $-90^{\circ} \leq \eta$ ,  $\alpha$ ,  $\gamma$ ,  $\delta \leq +90^{\circ}$ , decide upon the form of the potential, the strength is given by factor  $V_{\rm cf}$ . Energy eigenvalues, together with coefficients of wave functions, are obtained by diagonalisation of the  $16 \times 16$  matrices.

#### 3. Zeeman-effect Hamiltonian

By adding the energy of the Zeeman effect, the splitting of energy levels in a magnetic field  $B(B_x, B_y, B_z)$  can be calculated. The relevant Hamiltonian

$$H_{\rm mf} = g_J \mu_{\rm B} (B_x J_x + B_y J_y + B_z J_z) \tag{6}$$

does not introduce any new free adjustable parameters. For the ground state  ${}^{4}I_{15/2}$  of erbium, the Landé factor  $g_{J} = \frac{6}{5}$ .

#### 4. Luminescence spectra

Well-identified eight-line photoluminescence emission spectra are observed, among other substances, in zinc selenide and silicon [1,2]. From these spectra, the positions of the crystal-field states in the  ${}^{4}I_{15/2}$  spin-orbit ground state are constructed. An inspection of the level diagrams, as given in Figs. 1(c) and 2(c), suggests



Fig. 4. Crystal-field energy levels *E* in state  ${}^{4}I_{15/2}$  of the noncubic centre Si-Er-1 as a function of parameter  $\eta$  of tetragonal distortion,  $V_{cf} = 0.430$ ,  $\alpha = -1.7^{\circ}$ . Data points in averaged cubic symmetry are shown at  $\eta = 0^{\circ}$ . Best match to potential with tetragonal symmetry is at  $\eta = 16.4^{\circ}$ .

the presence of pairs of lines, which find their origin in a relatively small splitting of quartet levels in centres of near-cubic symmetry. On averaging the positions of line pairs, an analysis in cubic symmetry can be made [1]. The result is included in Figs. 1 and 2 in columns (a) and (b), and in Figs. 3 and 4 by the data points for  $\eta = 0$ . It can be concluded that satisfactory fits can be made. Also, with nearly equal values for the cubic field parameter  $\alpha$ , the two spectra show a strong similarity.

Actually, the eight-line spectra belong to centres of lower-than-cubic symmetry. The splitting of quartet levels in an axial field of tetragonal symmetry is shown in Figs. 3 and 4, including experimental level positions at the best adjusted value of parameter  $\eta$ , governing the balance of cubic and tetragonal potentials. To obtain best match of the calculated level positions, least squares adjustments were made to the experimental data of both spectra. Parameter sets are summarised in Figs. 1 and 2. For the ZnSe centre a monoclinic-I potential was found to give best agreement. The Si-Er-1 centre was fitted with orthorhombic-I symmetry; adding any monoclinic-I component deteriorated the result. Typical rootmean-square errors are around  $4 \text{ cm}^{-1}$ , therefore larger than the estimated experimental errors of around  $1 \,\mathrm{cm}^{-1}$ .

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# 5. Magnetic resonance spectra

With potential parameters determined from the optical spectra, the splitting of doublet levels in a magnetic field can be calculated in a straightforward manner with the Hamiltonian  $H_{mf}$  (Eq. (6)). Calculations were restricted to the regime of low magnetic field, in which the Zeeman effect is proportional to the magnetic field and, hence, the g tensors are constant. For centre ZnSe: Er<sup>3+</sup>, the monoclinic-I symmetry is in agreement with the reported spectrum [1]. However, the calculated principal values  $g_1 = 11.96$ ,  $g_2 = 2.45$  and  $g_3 = 4.86$  deviate substantially from values of the magnetic resonance spectrum labelled A. The identification of optical and EPR centres is thus not supported. For centre Si-Er-1, the calculated principal g values are  $g_{[0,0,1]} = 3.33$ ,  $g_{[1,1,0]} = 6.09$ and  $g_{[1,-1,0]} = 10.27$ . Evidently, the g tensor of an orthorhombic Si–Er-1 centre in silicon cannot be identified with the monoclinic-I EPR spectrum Si– OEr-1 reported recently [3]. In view of different production conditions of the erbium optical centres the result is not surprising.

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