Crystal-Field Energy Levels of Trivalent Erbium Ion in Cubic Symmetry

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This paper describes a scheme for the numerical calculation of crystal field (CF) energy levels and at the same time wave functions of the trivalent erbium ion in cubic symmetry. The 16-fold degenerate term $^4I_{15/2}$ of the trivalent erbium ion splits into three Stark quartets Γ_8 and two different doublets Γ_6 and Γ_7 (irreducible representations). The CF energy matrix of the Er^{3+} ion has been constructed and calculated from the complete diagonalization method, and the corresponding wave functions were used to calculate the ground state g-values. This method is outlined and illustrated by the examples of the Si:Er for comparison. The calculated g-factors are $g = 6.8$ and $g = 6.0$ for Γ_6 and Γ_7, respectively.

Key words: Crystal Field; Energy Level; Erbium; Rare Earth.

1. Introduction

Trivalent erbium ions (Er^{3+}) have played an important role in the development of optical communication technology [1, 2] in the last years. The transition from the first excited state $^4I_{13/2}$ to the ground state $^4I_{15/2}$ in Er^{3+} at 1.53 µm corresponds to an important telecommunication wavelength since standard silica based optical fibers have their maximum transparency at this wavelength.

When a rare earth (RE) ion is placed in a crystal lattice, it is subject to a number of forces which are absent in the free ion. These crystal forces are of very complex nature. There are, for instance, resonance interactions with neighbouring ions of the same kind, and there are electric and magnetic interactions with each individual ion in the vicinity.

The crystal field model has been very successful in the analysis of $4f^N$ configurations of rare-earth ions in solids [3 – 5], whose energy levels are reproduced through a Hamiltonian which involves both free-atom and crystal field operators.

The presence of the crystal field will modify the energy levels and wave functions of the free ions, and the determination of these modifications is subject of the crystal field theory. From a theoretical point of view, the rare earth elements are one of the most convenient fields for the elaboration and testing of the quantum theories of atomic spectroscopy and their application to an ion included in a crystal. These techniques allow the energy level scheme, deduced from experiment, to be simulated.

In a cubic field, the doublets Γ_6 and Γ_7 can be described by a spin Hamiltonian with an effective spin $S = 1/2$ and isotropic g-factors. For Γ_6 and Γ_7 belonging to the $J = 15/2$ state (Er^{3+} ion), the wave functions and, hence, g-factors are uniquely determined. A deviation from a pure LS-coupling somewhat changes these values. Moreover, such values of the g-factor may be observed if resonance occurs in a pure ground state; an admixture of the wave functions of excited states changes the value of the isotropic g-factor. The pattern of the electron paramagnetic resonance (EPR) of Er^{3+} ions in the Γ_6 and Γ_7 states in a cubic crystal field is closely similar to that in a lower symmetry field, since Γ_6 and Γ_7 correspond to Kramers doublets.

The aim of the present work is to establish the crystal-field energy levels and wave functions of Er^{3+} ion in cubic symmetry. The corresponding wave functions were used to calculate the ground state g-values. The calculations were performed by the MATLAB computer program.

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2. Calculations

If the RE ion is introduced into a crystalline matrix, the spin-orbit levels split further into CF levels under the action of the electric field provided by the crystal.

The CF Hamiltonian is most commonly expressed as

$$H_{\mathrm{CF}} = \sum_{n,m} B_n^m O_n^m, \tag{1}$$

where B_n^m and O_n^m are, respectively, CF energy parameters and Stevens operator equivalents which are expressed in powers of the components J_+, J_-, and J_z of the angular momentum operator [6]. Alternatively, it can be expressed in terms of CF coefficients A_n^m:

$$H_{\mathrm{CF}} = \sum_{n,m} A_n^m \langle r^n \rangle \theta_n O_n^m, \tag{2}$$

where $\langle r^n \rangle$ are radial averages over the $4f$-electron wave functions and θ_n are the Stevens coefficients α_J, β_J, γ_J for $n = 2$, 4, 6, respectively. These expressions are only valid for the CF split ground-state multiplet. The interaction represented in (1) or (2) splits the $(2J+1)$-fold degenerate ground-state multiplet into a series of CF energy level eigenvalues with energy E_i and corresponding eigenstate, labeled by its irreducible representation Γ_i.

For systems with cubic point symmetry there exists an ingenious and widely employed method (commonly referred to as Lea-Leask-Wolf (LLW) method) of parametrizing the eigenfunctions and eigenvalues of the CF Hamiltonian

$$H_{\mathrm{CF}} = B_4^0(O_4^0 + 5O_4^4) + B_6^0(O_6^0 - 21O_6^4) \tag{3}$$

by setting the two parameters required for the description of the CF in terms of parameters x and W defined by

$$B_4^0 F_4 = Wx \tag{4}$$

and

$$B_6^0 F_6 = W(1-|x|). \tag{5}$$

The operator equivalents O_n^m needed are as follows:

$$\begin{aligned}\beta_J\langle r^4\rangle O_4^0 = \beta_J\langle r^4\rangle \big[&35J_Z^4 - 30J(J+1)J_Z^2 \\ &+25J_Z^2 - 6J(J+1) + 3J^2(J+1)^2\big],\end{aligned} \tag{6a}$$

$$\beta_J\langle r^4\rangle O_4^4 = \beta_J\langle r^4\rangle \left[\frac{1}{2}(J_+^4 + J_-^4)\right], \tag{6b}$$

$$\begin{aligned}\gamma_J\langle r^6\rangle O_6^0 = \gamma_J\langle r^6\rangle \big[&231J_Z^6 - 315J(J+1)J_Z^4 \\ &+735J_Z^4 + 105J^2(J+1)^2J_Z^2 \\ &-525J(J+1)J_Z^2 + 294J_Z^2 - 5J^3(J+1)^3 \\ &+40J^2(J+1)^2 - 60J(J+1)\big],\end{aligned} \tag{6c}$$

$$\begin{aligned}\gamma_J\langle r^6\rangle O_6^4 = \frac{\gamma_J}{4}\langle r^6\rangle \big\{&\big[11J_Z^2 - J(J+1) - 38\big] \\ &\cdot (J_+^4 + J_-^4) + (J_+^4 + J_-^4)\big[11J_Z^2 - J(J+1) - 38\big]\big\}.\end{aligned} \tag{6d}$$

Here the values of the arbitary numerical factors F_4 and F_6 are chosen for convenience in each calculation. Tabulated values can be found in [7]. The parameter ratio can be expressed as

$$\frac{B_4^0}{B_6^0} = \frac{x}{1-|x|}\frac{F_6}{F_4}. \tag{7}$$

The coefficients B_4^0 and B_6^0 determine the magnitude of the crystal field splitting as a result of the arrangement of the surrounding cations and anions.

3. Results and Discussion

3.1. CF Interaction

The free Er^{3+} ion has an electron configuration $4f^{11}$ for which the lower term is $^4I_{15/2}$, and the first excited multilpet $^4I_{13/2}$, which is about 6500 cm^{-1} higher than $^4I_{15/2}$. In a cubic crystal field, the 16-fold degenerate term $^4I_{15/2}$ splits into three Stark quartets Γ_8 and two different doublets Γ_6 and Γ_7. The ground state in a cubic field can be one of the doublets (Γ_6 or Γ_7), whose relative position depends on the ratio between the fourth- and sixth-order terms in the crystal-field expansion.

The calculated energies, as obtained by a diagonalization of the appropriate CF Hamiltonian matrix given by (3), are summarized in Table 1 and the eigenstates of the ground state labeled by its irreducible representation Γ_6 and Γ_7 levels are:

$$\begin{aligned}\Gamma_6:\ &0.6333\left|\pm\frac{13}{2}\right\rangle + 0.5818\left|\pm\frac{5}{2}\right\rangle \\ &-0.4507\left|\mp\frac{3}{2}\right\rangle - 0.2394\left|\mp\frac{11}{2}\right\rangle\end{aligned} \tag{8}$$

Table 1. Observed and calculated energy levels (cm^{-1}) of the ground state $^4I_{15/2}$ and the first excited state $^4I_{13/2}$ for Si:Er.

Level	Refs. [8,9]		Ref. [10]	
	E (obs.)	E^a (cal.)	E (obs.)	E^b (cal.)
$^4I_{15/2}$	0	0	0	0
	71	76	78.8	79.4
	153	151	157.3	156.7
	244	243	249.3	252.7
	408	368	417.8	383.3
$^4I_{13/2}$	6498	6500	6504.8	6503.2

[a] CF parameters: $x = 0.35$ and $W = 0.8406\,cm^{-1}$
[b] CF parameters: $x = 0.35$ and $W = 0.8753\,cm^{-1}$

and

$$\Gamma_7:\ 0.5818\left|\pm\frac{15}{2}\right\rangle + 0.3307\left|\mp\frac{7}{2}\right\rangle + 0.7181\left|\mp\frac{1}{2}\right\rangle + 0.1909\left|\mp\frac{9}{2}\right\rangle. \quad (9)$$

The calculated energy levels with spin $J = 13/2$ in a cubic crystal field as a function of parameter x for $W = 0.8406\,cm^{-1}$ are given in Figure 1. These levels are labeled according to the convention for T_d symmetry.

Figure 2 shows the energy levels E in the state $^4I_{15/2}$ as a function of the parameter x. 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 energies of the Γ_8 levels vary nonlinearly with the crystal field parameter x. Always five levels are obtained: two doublets belonging to the Γ_6 and Γ_7 irreducible representations, respectively, and three quartets of Γ_8 symmetry type.

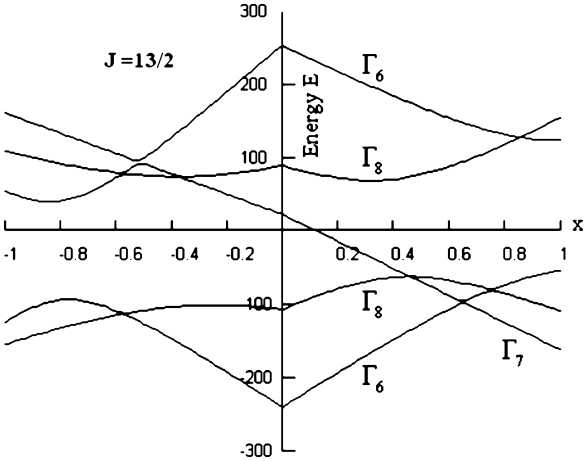

Fig. 1. Calculated energy levels with spin $J = 13/2$ in a cubic crystal field as a function of parameter x for $W = 0.8406\,cm^{-1}$.

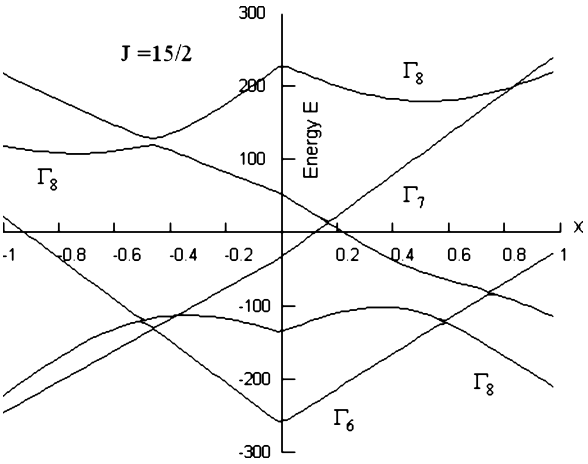

Fig. 2. Calculated energy levels with spin $J = 15/2$ in a cubic crystal field as a function of parameter x for $W = 0.8406\,cm^{-1}$.

The energy levels (cm^{-1}) were performed by the MATLAB computer program and are listed in Table 1. We have also included in this table the experimental CF levels of the Si:Er [8 – 10] for comparison. The positions of the Stark levels vary with the host. It can be seen that the calculated crystal field energies are consistent with the observed ones.

Actual calculations were performed with scaling factors $F_4 = 60$ and $F_6 = 13\,860$ for $J = 15/2$ and $F_4 = 60$ and $F_6 = 7560$ for $J = 13/2$.

3.2. Zeeman Effect

The Zeeman splitting of about 0.1 meV induced in an EPR experiment in the K-band (frequency 23 GHz) is only a small perturbation on the states formed after spin-orbit and crystal-field interactions. Energies of the $J = 15/2$ spin-orbit ground state sublevels are calculated in the presence of a crystal field and a magnetic field. The energy of the Zeeman effect is calculated by applying the operator

$$H_Z = g_J \beta H J. \quad (10)$$

Where g_J is the Landé factor and β is the Bohr Magneton.

By the magnetic field the degeneracy in the crystal-field quartet and doublet levels is lifted. The g-factor g

can be calculated from the following expression:

$$g = 2g_J \langle \Gamma_i | J_z | \Gamma_i \rangle . \quad (11)$$

The calculated g-factors according to (8) and (9) are $g = 6.8$, $g = 6.0$ for Γ_6 and Γ_7, respectively.

It is important to note here that the g-value depends directly on the coefficients in the wave functions (see (8) and (9)).

The calculated g-value (6.0) for Γ_7 of this work is in better agreement with the observed values (close to 6) of Er^{3+} ion in various semiconductors [11 – 13].

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